

SITE-Emerging Technologies:
Laser Induced Photochemical Oxidative
Destruction of Toxic Organics in Leachates
and Groundwaters

by

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FOREWORD

The U.S. Environmental Protection Agency (EPA) is charged by congress with protecting the Nation's land, air, and water resources. As the enforcer of national environmental laws, the EPA strives to balance human activities and the ability of natural systems to support and nurture life. A key part of the EPA's effort is its research into our environmental problems to find new and innovative solutions.

The Risk Reduction Engineering Laboratory (RREL) is responsible for planning, implementing, and managing research, development, and demonstration programs to provide **an** authoritative, defensible engineering basis in support of **the** policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and superfund-related activities. this Publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

Now in its sixth year, the Superfund Innovative Technology Evaluation (SITE) Program is part of EPA's research into cleanup methods for hazardous waste sites around the nation. Through cooperative agreements with developers, alternate or innovative technologies are refined at the bench-and pilot-scale level and then demonstrated at actual sites. EPA collects and evaluates extensive performance data on each technology to use in remediation decision-making for hazardous waste sites.

This reports documents the results of laboratory and pilot-scale field testing of Laser Induced Photochemical Oxidative Destruction of toxic wastes in groundwater. It is the first in a series of reports sponsored by the SITE Emerging Technologies Program.

E. Timothy Oppelt, Director
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ABSTRACT

Laser Induced **Photochemical** Oxidative Destruction of Toxic Organics in Solution

Organic compounds and specifically chlorinated aromatic and unsaturated organics are major contaminants in groundwaters. These latter species also tend to rank high on the list of EPA priority pollutants, even at the low (ug/l) concentrations that they are normally found in groundwaters. The technology described in this report has been developed under the Emerging Technologies section of the Superfund Innovative Technology Evaluation (SITE) Program to photochemically oxidize organic compounds in wastewater by applying ultraviolet radiation using an excimer laser. The photochemical reaction is capable of producing the complete destruction of moderate to extremely low concentrations of toxic organics in water. The energy supplied by the laser is sufficient to stimulate photochemical reactions between the organics and hydrogen peroxide employed as a chemical oxidant, causing photo-oxidation and/or phototransformation of the toxic species to carbon dioxide, water, and the corresponding halogenated acid. Additionally the radiation is not absorbed to any significant extent by the water molecules in solution. The process has been developed as a final treatment step to reduce organic contamination in groundwater and industrial **waste** waters to acceptable discharge limits.

Optimum conditions for the complete destruction of several different classes of compounds were developed and demonstrated in the laboratory.

This report is submitted in fulfillment of cooperative agreement number CR-815330-02-0 by Energy & Environmental Engineering, Inc. under partial sponsorship of the USEPA. This report covers the period from October 1988 to September 1990, with the completion of work in September 1990.

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I EXECUTIVE SUMMARY

In the two-year period from October 1988 to September 1990, Energy and Environmental Engineering, Inc. conducted a laboratory investigation of a new process for destroying toxic organic compounds in dilute waste water solutions. In this process, Laser Induced Photochemical Oxidative Destruction (LIPOD), solutions containing 10 to 200 ppm of organic compounds were irradiated with laser generated ultraviolet radiation in the presence of the oxidant hydrogen peroxide.

The effects of organic concentration, irradiation exposure, wavelength and oxidant concentration on the destruction efficiency were determined for a series of representative organic contaminants, and a preliminary design for a larger scale process was completed.

Summary of Results

The experiments showed that the LIPOD process is capable of destroying from 90 to 99 percent of the organic contaminants in dilute waste water solutions. The destruction process occurs in two steps. Some of the contaminant is destroyed during the irradiation period of about one minute. The destruction continues after the solution is removed from the radiation field for a period of hours until essentially complete destruction is achieved.

Economic comparison of the LIPOD process with competitive processes indicates **that the** LIPOD process can offer significant cost savings over other ultraviolet treatment processes and carbon adsorption.

II INTRODUCTION

The Superfund Innovative Technology Evaluation (SITE) Program was implemented to accelerate the development and application of innovative cleanup **technologies at** hazardous waste sites across the country. The SITE Program is comprised of the following five component programs:

- . Demonstration Program
- . Emerging Technologies Program
- . Measurement and Monitoring Technologies Development Program
- * Innovative Technologies Program
- . Technology Transfer Program

This report summarizes the results of a two-year bench-scale evaluation of the Laser Induced Photochemical Oxidative Destruction (LIPOD) process, sponsored by, the SITE Emerging Technologies Program.

The LIPOD process is based on the photochemical destruction of toxic organic chemicals in dilute aqueous solutions. Energy supplied by an excimer laser is absorbed by the organic molecules, rendering them oxidizable by the oxidant hydrogen peroxide which is added to the solution. The advantage of this process is that the narrow band ultraviolet radiation is preferentially absorbed **by** the organic molecules and hydrogen peroxide, with little being absorbed by the surrounding water molecules.

Aromatic and aliphatic organic compounds, and particularly chlorinated organics, are major contaminants in ground waters at or near hazardous waste sites. These species also rank high on the Environmental Protection Agency's (EPA) list of priority pollutants, even at the parts per billion concentrations often found in the waste waters. Because of the very low concentrations, detoxification of these waters is difficult and expensive. Carbon adsorption and **UV** ozonation are currently in use. The LIPOD process shows promise of better performance at a lower cost.

III CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

Laboratory scale testing of the **LIPOD** process has shown that the process is capable of destroying 90 percent or more of toxic organic compounds in dilute water solutions. The effects on destruction efficiency of organic concentration, oxidant concentration and irradiation dosage have been determined for a series of representative organic compounds. On the basis of these results, the cost of a commercial scale process has been estimated and found to be very competitive with existing technologies which are now in use for waste water detoxification.

The chemistry of the LIPOD process proceeds in two steps, an initiation step followed by a propagation step. In the initiation step, some destruction of the organic occurs during the short duration of the irradiation. When the solution is removed from **the** radiation field, propagation of the oxidative destruction continues over a period of hours until more than 90 percent of organic has been destroyed.

RECOMMENDATIONS

Results to date suggest that the LIPOD process has excellent potential for effective removal of organics from dilute waste waters and that further development of this process is warranted. Treatability studies in the laboratory using actual waste water samples from hazardous waste sites are needed to establish how the process performs on waste containing a variety of organic compounds and inorganic salts. Successful completion of these treatability studies would lay the groundwork for larger scale field testing of the process.

IV BACKGROUND INFORMATION

A. Process Description

Laser Induced Photochemical Oxidative Destruction (LIPOD) is a process developed at Energy and Environmental Engineering, Inc. (E3I) to oxidize low levels of toxic organics in contaminated waters to non-toxic species. The process has been under development for the past seven years, and its efficacy relies on the use of a coherent electromagnetic radiation source in the UV portion of the spectrum to activate an exothermic process in the presence of an oxidant so as to initiate a chain oxidation reaction. The UV source is an excimer laser which provides a high intensity, coherent energy source. The oxidant is hydrogen peroxide which is miscible with water in all proportions and thus provides sufficient oxygen and or hydroxyl radicals to completely oxidize the toxic molecules.

Unlike other **UV** irradiation processes in which the toxic molecules must be exposed continually to the **UV** radiation with both hydrogen peroxide and ozone present as chemical oxidants, this process requires no ozone and the contaminant is exposed to the **UV** light source only for a very **short** time (< 50sec) to initiate the oxidative chain reaction. Our investigations have shown that only a portion of the fluid to be decontaminated needs to be exposed to the **UV** radiation source in the presence of hydrogen peroxide. This exposed fluid can be contacted with unexposed fluid and additional hydrogen peroxide and the entire fluid pool will undergo the chain oxidation reaction.

A typical process flow scheme is shown in Figure 1, the feed stream containing the toxic species and the chemical oxidant, hydrogen peroxide, flow countercurrent to the laser beam in a photochemical reactor where the toxic compounds are irradiated. The overall reaction chemistry is depicted in Figure 2. When oxidizing halogenated organics, the reaction byproducts are carbon dioxide, water, and the corresponding halogen acid.

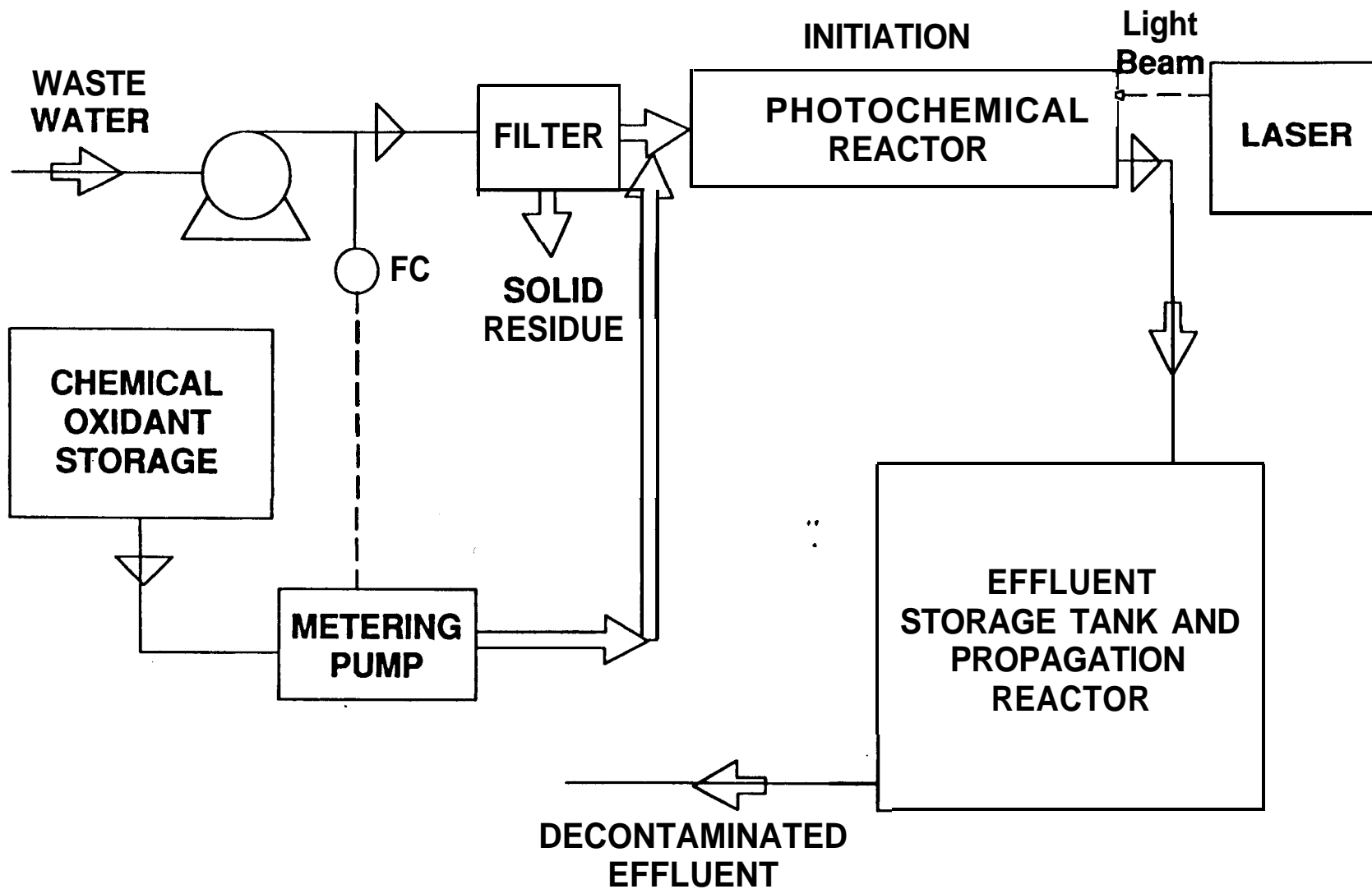


Figure 1. Process Flow Scheme

- . UV Coherent Light Source
- . Photolysis Reactor
- . Oxygen Source



Figure 2. Overall Reaction Chemistry

B. Potential Application

1. Introduction

Since the industrial revolution in the United States, industrial waste products have been generated in ever increasing amounts and, in general, have been discarded in a very haphazard manner. Little thought was given to the suitability of the industrial and municipal landfills that were typically used for disposal. The Times Beach and Love Canal cases have dramatically illustrated the folly of past practice.

In the 1970s, increasing public concern with the quality of the environment led to federal legislation to manage newly generated hazardous wastes as well as a separate program to deal with the cleanup of existing uncontrolled waste sites. This legislation is commonly known as the Resource Conservation and Recovery Act (RCRA) of 1976 and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) of 1980, respectively. CERCLA established the Superfund program to provide a mechanism for expeditious cleanup of the worst of these sites and has provided the focal point for marketing a wide range of services involved with the cleanup effort.

Ground water contamination at hazardous waste sites results from leaching action from those landfills containing hazardous materials and can be composed of a variety of toxic organics. Among the most difficult of these to deal with are a class of chemicals known as aromatic organic compounds. They are pervasive: they are not biodegradable; they are among the most toxic chemicals to be dealt with in the Superfund Program; and they do not lend themselves to simple destruction techniques.

In addition to the cleanup of Superfund sites, a market exists for the neutralizing of toxic wastes in those industries that can no longer dump their waste products in landfills or discharge contaminants into water streams. To a large extent, these industries have been able to recycle the hazardous chemical compounds, but small amounts of these materials must be destroyed prior to release of the effluent to the environment.

2. Superfund Sites

The clean up of existing hazardous waste sites represents one of the most difficult and costly problems facing our society over the next fifty years. The clean up activity associated with the Superfund program is estimated by the Office of Technology Assessment to be more than \$100 billion with the cost of treating ground water contamination comprising more

than 50 percent of the total.

Typically, the ground water at these sites will contain trace amounts of organic contaminants that have leached from old landfills. The ground water clean up program will normally consist of the following elements:

- * Taking measures to prevent further leaching of contaminants into the aquifer.
- * An assessment of the plume of contamination in the aquifer as well as the nature and amounts of contamination.
- * Removal and treatment of contaminated groundwater with the treated water either discarded or returned to the aquifer.

Much of the early effort at cleanup has involved relocation, removal, or on-site containment of hazardous materials and not permanent destruction. To some extent, this only serves to transfer the problem to another location to be dealt with another day. The expressed desire is for destructive treatment or a permanent stabilization of the hazardous materials. However, little progress has been made toward this end, particularly for the expensive, difficult and uncertain task of contaminated waste and ground water cleanup.

The LIPOD process is well suited to the ground water cleanup problem. It is capable of destroying the low levels of organic contaminants normally found at a lower cost than competing processes. LIPOD represents a vast improvement in the currently available technologies because it:

- * More effectively destroys organic compounds than competing technologies.
- * Does not require significant post treatment as do competing physical separation technologies.
- * Can be built in such a manner as to be easily transported and operated at individual waste sites.

3. Industrial Waste Streams

The Resource Conservation and Recovery Act of 1976 (RCRA), as amended by the Hazardous and Solid Waste Amendments of 1984 (HSWA) prohibits continued placement of RCRA regulated wastes in or on the land, including placement in landfills, land treatment areas, waste piles, and surface impoundments. This has resulted in the need for new waste management techniques

to deal with the 3-5 billion gallons of waste solvents generated annually. Additionally each year about 70 billion pounds of chemicals considered hazardous under RCRA are used in the United States. Of this, about 80 percent are organic compounds used in pesticide formation; paint and adhesives; cleaning; and chemical intermediates. Of the hazardous materials to be treated the treatment process chosen for use will normally be custom designed for each application and will depend on the following:

- * The type of chemical involved
- * The concentration of the waste stream
- * The potential uses for recovered chemicals

In most cases, an aqueous stream containing trace amounts of contaminants must be treated further prior to unrestricted release to the environment. Present practice, in most cases, is to use activated charcoal post treatment for these waste streams. In some cases, this will remain the best practice. However, for most of the organic compounds encountered, the LIPOD process will be more cost effective.

C. Competitive and Complementary Technologies

The technologies described below can also be used to treat contaminated waste waters. They may be used prior to LIPOD treatment to reduce high concentrations of contaminants, or they may be competitive with the LIPOD process in treating very dilute solutions, or they may be used after the LIPOD process to capture organics that may not be easily destroyed by the LIPOD process (e.g. aliphatic saturated and conjugated organic compounds).

1. Physical Treatment Processes.

These processes are based on physical methods of separation and generally do not result in destruction of the contaminants in the waste feed stream. The most common of these processes are distillation, stripping, and adsorption.

Distillation processes are applicable to high organic content wastes but usually generate a large volume residual that contains appreciable organic contamination. Incineration is often the principal means of handling this type of residual.

Air stripping is generally used on Waste streams containing low levels of volatile contamination with steam stripping suitable for streams containing somewhat higher levels of contamination. However, some level of residual contamination requiring additional treatment can often be expected from

these technologies.

Carbon and resin adsorption are commonly used to remove trace amounts of contaminants to achieve low organic concentration levels. The adsorptive materials will contain the contaminants and must either be incinerated or put through a restorative process leaving a slurry mixture that can be incinerated.

2. Chemical Treatment Processes.

Most of the chemical processes of interest for the treatment of organic hazardous wastes make use of oxidation to render the wastes harmless. The methods use either high temperature conditions or a catalyst to bring this about.

The Wet Air Oxidation process and a somewhat similar Supercritical Water Oxidation process cause reaction of the organic contaminants with free oxygen in the waste stream by raising the temperature and pressure of the aqueous wastes to very high levels. The organic materials are generally converted completely to carbon dioxide and water by these processes.

UV/ozonolysis and other oxidation processes such as peroxide, potassium permanganate, and hydrogen peroxide treatments do not normally achieve total destruction and must be considered as a pretreatment step for a second treatment technology, usually a biotreatment process.

3. Biological Methods.

Biological treatment processes used for the removal of organic solvents and other volatile organic compounds from industrial waste streams can be divided into two major categories: (1) aerobic processes, and (2) anaerobic processes. In aerobic systems, microorganisms use oxygen to biologically oxidize compounds. Anaerobic, or oxygen-free, biotreatment systems make use of a reducing metabolic process. Typically a series of reactions involving acetogens (acid generating) and methanogenic bacteria cause organic compounds to be broken down into methane and simple organic acids.

Each of these processes can be further subdivided into suspended growth or attached growth systems. Suspended growth systems are characterized by microbes moving freely within the waste stream or being suspended by mechanical agitation. Attached or "fixed film" growth systems have layers of microbes attached to a suitable medium that comes into surface contact with the waste stream.

Aerated treatment systems are generally open surface impoundments which require large land areas and considerable capital investments. Aerated processes have the potential to produce significant air (and odiferous) emissions. Being open to the environment, the treatment plants are subject to weathering and their design features and biological kinetics are stressed by precipitation and temperature extremes,.

4. Incineration.

Incineration is the principal disposal alternative for nonrecoverable, flammable solvent hazardous wastes. Incineration possesses several advantages as a hazardous waste disposal technology, including the following:

- **Thermal destruction** by incineration provides the ultimate **disposal of** hazardous wastes, minimizing future liability from land disposal:
- Toxic components of hazardous wastes can be converted to harmless or less harmful compounds:
- The volume of waste material may be reduced significantly by incineration: and
- Resource recovery (i.e., heat value recovery) is possible through combustion.

While incineration as a hazardous waste management technique possesses many potential advantages, there are also two major potential drawbacks: environmental impacts and costs. Incineration has the potential to affect both air and surface waters via stack emissions and fugitive emissions of volatile compounds, and the production of solid wastes (ash and scrubber liquors and scrubber sludge).

Incineration facilities permitted to operate by EPA under the provisions of RCRA are required to meet environmental standards in the following areas:

- They must meet destruction and removal efficiency (DRE) standards.
- They must meet standards for the release of acid gasses from the stack, including HCl.
- They **must** meet standards **for the** emission of particulates from the stack.
- They must meet standards for limitation of emission of toxic air pollutants (e.g., toxic metals) from **the** stack.

Costs of incineration are higher than most hazardous waste management alternatives. Incineration costs more **because of** the large energy input requirements and the high cost of environmental controls. These costs vary widely depending upon waste characteristics, incinerator design, and various operational considerations.

V EXPERIMENTAL RESULTS

A. Experimental Procedures

Laser destruction experiments were carried out on a series of hydrocarbons in dilute solutions, using air, dissolved oxygen, sodium nitrate, and hydrogen peroxide as oxidants.

The performance of these processes was measured in terms of its ability to destroy toxics, relative to the maximum achievable toxic destruction capability. This capability is measured as the difference between relative destruction with the light on and with the light off.

The relative destruction achieved is defined as:

$$E = \frac{C_{in} - C_{out*}}{C_{in}} \quad \frac{C_{in} - C_{out}}{C_{in}}$$

where C_{in} = Inlet Feed Toxic Concentration to reactor

C_{out*} = Outlet Feed Toxic Concentration, with Irradiation

C_{out} = Outlet Feed Toxic Concentration, no Irradiation
which **is the** relative destruction of the toxic with the **light** on less the destruction obtained in the absence of **light**. This latter term accounts for evaporation, absorption and other processes which can occur in the absence of light.

The maximum achievable value of E, (E_{max}), is obtained when $C_{out} = 0$.

The process performance is then measured in terms of the destruction efficiency, defined as E/ E_{max} .

In terms of concentrations, the expression reduces to:

$$\text{Percent destruction achieved} = 100X \frac{E}{E_{max}} = 100 X \frac{C_{out} - C_{out*}}{C_{out}}$$

This term is a conservative measure of process performance and is used for all the data presented herein.

In the results reported, the percent of destruction achieved was determined as a function of:

- . Toxic Compound speciation
- . Oxidant speciation
- . Aqueous concentration of toxic
- . Concentration of oxidant
- . Irradiation Dosage
- . Irradiation wavelength, and
- . Time

To assist in the understanding of the results, absorbance coefficients were measured for each of the hydrocarbons studied, and for a number of common ionic species which might be present in contaminated waste water.

A Lambda Physik, excimer laser was used to produce the coherent light source. The laser was calibrated and optimized to produce energy at specific wavelengths. The laser was calibrated daily before each experimental run, monitoring the input energy to the reactor and the output energy from the reactor.

Analysis of the toxic solutions before and after irradiation was performed on a Hewlett Packard 1090 HPLC. The HPLC was calibrated daily before each run and compared to a five point calibration curve generated for each organic compound. Preparation of standards and HPLC analysis were performed in accordance with the methods approved by the EPA in the final QA/QC plan accepted by the EPA for chemical analysis of water and waste water. Water blanks and 50 ppm solutions of the toxic compounds as standards were all analyzed before each experimental batch of irradiated samples, thus, ensuring some degree of accuracy and precision in the observed toxic concentration changes.

Toxic concentration changes in the water solutions, by-products, and column effluents were determined and monitored by observing any changes on the five point calibration curves generated for each of the toxic species. Complementary analyses were carried out in our GC/MS laboratories on the pure and irradiated samples to identify any irradiated products, while observing the changes in initial toxic

concentrations

The HPLC system used included a reversed phase RP18 Lichospher 100, 5 micron column with 100 by 2.1 mm dimensions and a variable wavelength Diode Array UV Detector. Irradiated samples were collected in duplicate at five time intervals of 0,10,30,50,& 80 minutes. Upon collection the samples were analyzed on the HPLC and then stored in amber colored vials. The samples in the vials were monitored over time to determine the continued destruction.

50 ppm solutions of the toxic compounds were made up in a 17 liter bottle. The solutions were fed to the photochemical reactor by a variable speed peristaltic pump, set at 30 ml/min. When using hydrogen peroxide as the oxidant **the** toxic solutions were mixed at a mixing tee with the peroxide solution and then fed into a 1 meter by 2.3 cm by 0.8 cm flow reactor. The solutions flowed countercurrent to the laser beam and were irradiated in the reactor. The irradiated samples were then collected from an exit port in amber colored vials with teflon lined caps for analysis.

Total organic carbon (TOC) analysis was carried out on the duplicate samples collected, on a Dohrman carbon analyzer, which measures any change in the total organic carbon content of a compound **as** the reaction proceeds over time.

PH measurements were continuously taken of the toxic solutions before and after irradiation.

Toxic Components

The compounds listed in Table 1 were selected as representative of toxic organics found in waste water. UV absorbance was measured for each compound in the concentration range of 10 to 200 ppm. Absorbance values are shown in Table 1. The absorbance measurements were carried out in the 190 to 250 nm range of the spectra on a **UV**spectrophotometer. The absorbance **at the** standard irradiation wavelength is reported in Table 1.

Table 1. Toxic Concentration and Absorbance

Toxic Compound	Concentration, ppm	Absorbance
Chlorobenzene	50	1.49
Dichloroethene	50	1.30
Dichloroethane	50	0.33
Benzidene	50	1.44
Hexanoic Acid	50	0.41
Bis-2-chloroethylether	50	0.37
Methyl Ethyl Ketone	50	0.38

Chlorobenzene Conc.	Absorbance
200	1.580
150	1.548
100	1.526
50	1.492
10	1.260

Additionally the absorbance at the standard wavelength of 100 ppm solutions of some common ionic species which may be present in contaminated waste water were also obtained, (Table 2).

Table 2. Ionic Species Concentration and Absorbance

Ionic Species	Concentration, ppm	Absorbance
Magnesium Chloride	100	0.614
Magnesium Sulphate	100	0.289
Magnesium Nitrate	100	1.546
Sodium Chloride	100	0.751
Sodium Sulphate	100	0.609
Sodium Nitrate	100	1.560
Calcium Chloride	100	0.727
Calcium Sulphate	100	0.362
Calcium Nitrate	100	1.564
Water		0.253

Table 1 results showed that Benzidine, t-Dichloroethene and Chlorobenzene exhibited high absorbances, Hexanoic Acid and Methyl Ethyl Ketone showed modest absorbance values while Bis-2-Chloroethyl Ether and t-Dichloroethane showed low absorbances.

The absorbances of the ionic species showed very low absorbance values in aqueous solutions and except for solutions containing nitrates, the **spectral values** were not significantly different from that of pure water. Therefore, only nitrate containing solutions were expected to have any adverse or impeding effect on the process. This adverse effect may be overcome by shifting the irradiation wavelength. Because of its high absorbance coefficient, chlorobenzene at 50 ppm concentration was selected as the representative compound on which most of our experimental studies were carried out.

50 ppm solutions of chlorobenzene were made up and a five point calibration curve established, from which all concentration changes were measured. Analysis and close monitoring of the standard 50 ppm solution with time showed that even after a 3 month period the concentration had only changed by a factor of < 10%. This enabled us to monitor concentration changes of the laser irradiation process during irradiation and for long periods after, since there was not a significant change in the standard 50 ppm solution.

The standard 50 ppm solutions were run on the HPLC before and after each set of the irradiated samples were analyzed each day. It was observed **that there** was no significant changes in the standard with

time, thus changes that were observed in the samples were due to the laser stimulated reactions initiated by the LIPOD process.

B. Initial Irradiation and Oxygenation Experiments.

Initial experiments on the process were carried out employing various concentrations of chlorobenzene solution in a batch mode using a quartz cell. The emphasis of these tests was to obtain samples of the irradiated toxics to determine the formation of any by-products, and to establish run conditions and equipment design for the continuous flow system. As these experiments were exploratory and preliminary in nature, a batch cell system was used, thereby avoiding complications that could arise from a continuous flow system.

The oxidation process was initially thought to be produced by dissolved oxygen in solution. Calculations summarized in Table 3 show the maximum extent of reaction that should be achievable with various toxic species as is limited by saturated oxygen dissolved in solution. Table 4 and Figure 3 show the destruction obtained for air saturated chlorobenzene solutions at different concentrations and irradiation dosages. These results indicated that at very low toxic concentrations <12.5 ppm, competitive absorption takes place between the water and the toxic molecules. Under these conditions the ratio of light absorbed by the water molecules to the light absorbed by the toxic molecules becomes an important limiting factor in the photolysis process. At higher toxic concentrations >50 ppm the amount of oxygen dissolved in the solution is too low to allow complete oxidation of the toxics. Therefore best results were achieved at concentrations between 12.5 and 50 ppm.

These results led us to investigate two schemes for effectively oxidizing the toxic solutions, recycle aeration and chemical oxygenation. The baseline case against which all of the oxygenation methods were compared, is the system shown in Figure 4 where the feed solution is saturated with air but no further aeration occurs. For all of the aeration experiments, 50.0 ppm chlorobenzene solutions were fed into the system and irradiated at 0 (method Blank), 1, 3, 5, and 10 photons per molecule. Figure 5 shows a schematic of the recycle aeration system, using air and pure oxygen as the oxidant.

Aerated Recycle Systems

In cases where the oxidant was insoluble in water (air, oxygen) aeration rates were achieved by aerating a recycle stream to its saturation value and then controlling the recycle rate. At 0.208 atm and 70°F, the oxygen concentration in an oxygen saturated solution is 2.9×10^{-7} gmmoles/cc, based on the Henry's law constant. In this system the feed solution flows in the reactor

Table 3

Table 3. Calculation of Maximum Extents of Reaction as limited by dissolved oxygen

Basis: Toxic + aO₂ --> bH₂O + cCO₂ + dHCl + e NO₂

Oxygen saturation concentration = 2.90E-07 gmol/cc

TOXIC	a	M	Toxic Conc. (12.5 PPM) gmol/cc	Maximum Extent of Reaction *
Chlorobenzene	7.0	112.56	1.11E-07	0.37
Benzidine	17.0	184.20	6.79E-08	0.25
Dichloroethane	2.5	98.96	1.26E-07	0.92
Dichloroethene	2.0	96.96	1.29E-07	1.00
Hexanoic Acid	9.0	116.10	1.08E-07	0.30
Bis-2-Chloroethyl Ether	5.0	142.40	8.78E-08	0.66
Methyl Ethyl Ketone	5.5	72.10	1.73E-07	0.30

Toxic	a	M	Toxic Conc. (12.5 PPM) gmol/cc	Maximum Extent of Reaction *
Chlorobenzene	7.0	112.56	4.44E-07	0.09
Benzidine	17.0	184.20	2.71E-07	0.06
Dichloroethane	2.5	98.96	5.05E-07	0.23
Dichloroethene	2.0	96.96	5.16E-07	0.28
Hexanoic Acid	9.0	116.10	4.31E-07	0.07
Bis-2-Chloroethyl Ether	5.0	142.40	3.51E-07	0.17
Methyl Ethyl Ketone	5.5	72.10	6.93E-07	0.08

a = Stoichiometric coefficient of oxygen for oxidation reaction

M = Molecular weight of toxic compound

PPM = Parts per million, mass:mass

* Reaction extents for oxidation reactions are calculated as follows

$$\text{Extent of reaction} = \frac{\text{[Moles Oxygen Present]}}{\text{[Moles Oxygen Required for Oxidation]}}$$

Table 4

Table 4. Batch Photolysis of Chlorobenzene Solutions Saturated with Air

$$\frac{C_{\text{outlet}}}{C_{\text{inlet}}} \text{ at Various Inlet Concentrations}$$

		C_{inlet}			
		3.125	12.5	50	100
		$\frac{C_{\text{out}}}{C_{\text{inlet}}}$			
Photons	1	0.53	0.43	0.49	0.72
-----	3	0.39	0.2	0.29	0.72
molecule	5	0.37	0.09	0.15	0.58
	10	0.24	0.06	0.09	0.22
		$1 - \left(\frac{C_{\text{out}}}{C_{\text{inlet}}} \right)$			
Photons	1	0.47	0.57	0.51	0.28
-----	3	0.61	0.8	0.71	0.28
molecule	5	0.63	0.91	0.85	0.42
	10	0.76	0.94	0.91	0.78

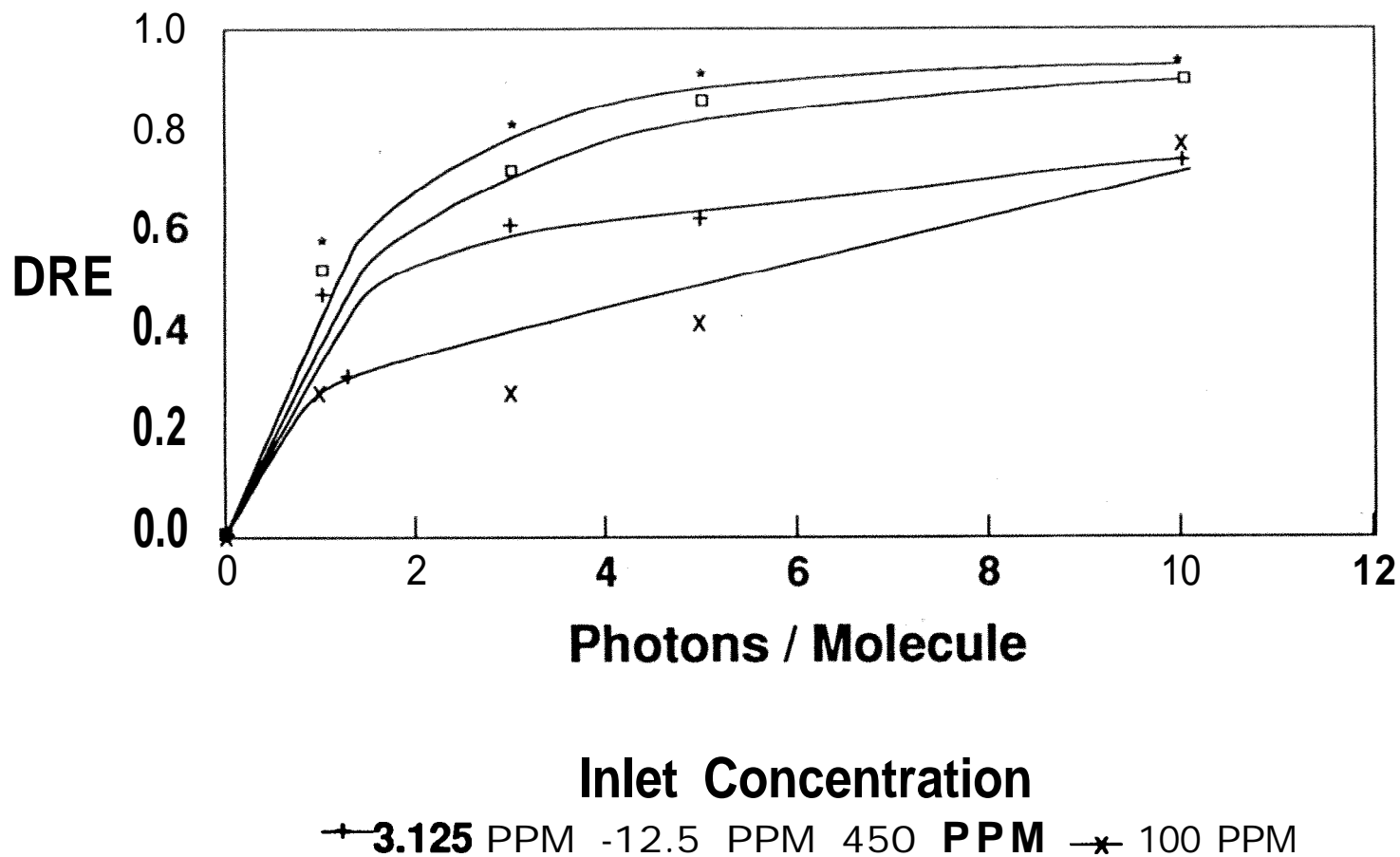


Figure 3. Impact of Irradiation Dose and Inlet Concentration On Extent of Reaction (Chlorobenzene saturated with air)

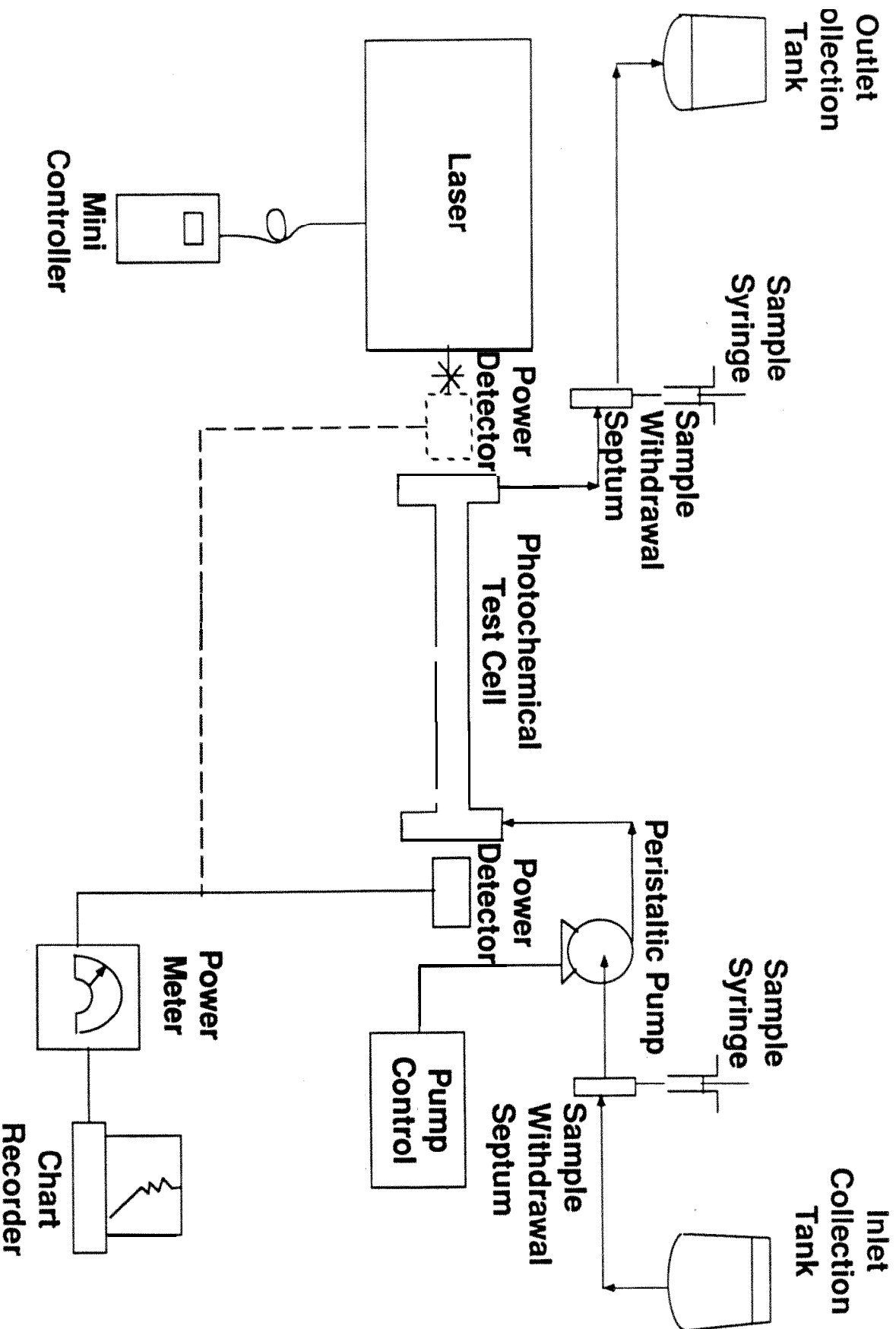


Figure 4. Schematic of Test Facility for Non-Aerated Fluids

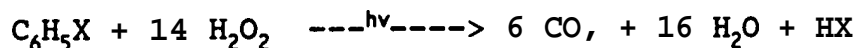
dissolved in the feed solution, takes place at the inlet end of the reactor. The bulk of the reaction, however, occurs at the interface of the mixing zone between the toxic and the aerated recycle fluids near the light admission port of the reactor. The irradiated and reacted fluid leaves the reactor and is split into two streams, a recycle stream and a product stream. The concentration of air and/or oxygen in the recycle stream is restored to saturation levels by the aerator. The recycle rate is controlled independently of the toxic solution feed rate, and thus controls the rate of oxygen to toxic in the reaction zone:

Chemical Oxygenation

The next oxygenation technique examined was that of chemical oxygenation employing hydrogen peroxide and sodium nitrate as the oxygenating source, (Figure 6).

First considering Sodium Nitrate, absorbance experiments indicated that aqueous solutions of dissolved sodium nitrate, absorbs energy in the ultraviolet region of the spectrum. It was further known that nitrates can act as electron acceptors, and so could act as an oxidant for the toxic solutions. Since sodium nitrate is highly soluble in water, the problem of dissolved oxygen solubility limitation could be overcome with the use of the sodium nitrate as an oxygen carrier. In these experiments, 50ppm solutions of a mixture of sodium nitrate and chlorobenzene were fed into the reactor and irradiated.

The next experiments were conducted with hydrogen peroxide as the chemical oxidant. In these experiments (Figure 6) hydrogen peroxide is mixed at a mixing tee with the toxic solutions prior to entering the reactor. The mixed solutions of hydrogen peroxide and toxic then flows down the reactor towards the laser. The hydrogen peroxide is very soluble in aqueous solutions and the oxidant level can be set at any desired value. The general chemical reaction equation, involving hydrogen peroxide as the oxidant is shown in Figure 2,



and was used to determine stoichiometric requirements.

For each experiment run, the laser pulse frequency and toxic feed flow rate were set to deliver the desired irradiation dosage of 0,1,3,5, and 10 photons / molecule. The toxic and oxidizing agent concentrations were continuously monitored at the feed and effluent ports by the HPLC. The irradiated and non-irradiated reactor effluent were collected and analyzed within thirty minutes after the samples were collected from the reactor.

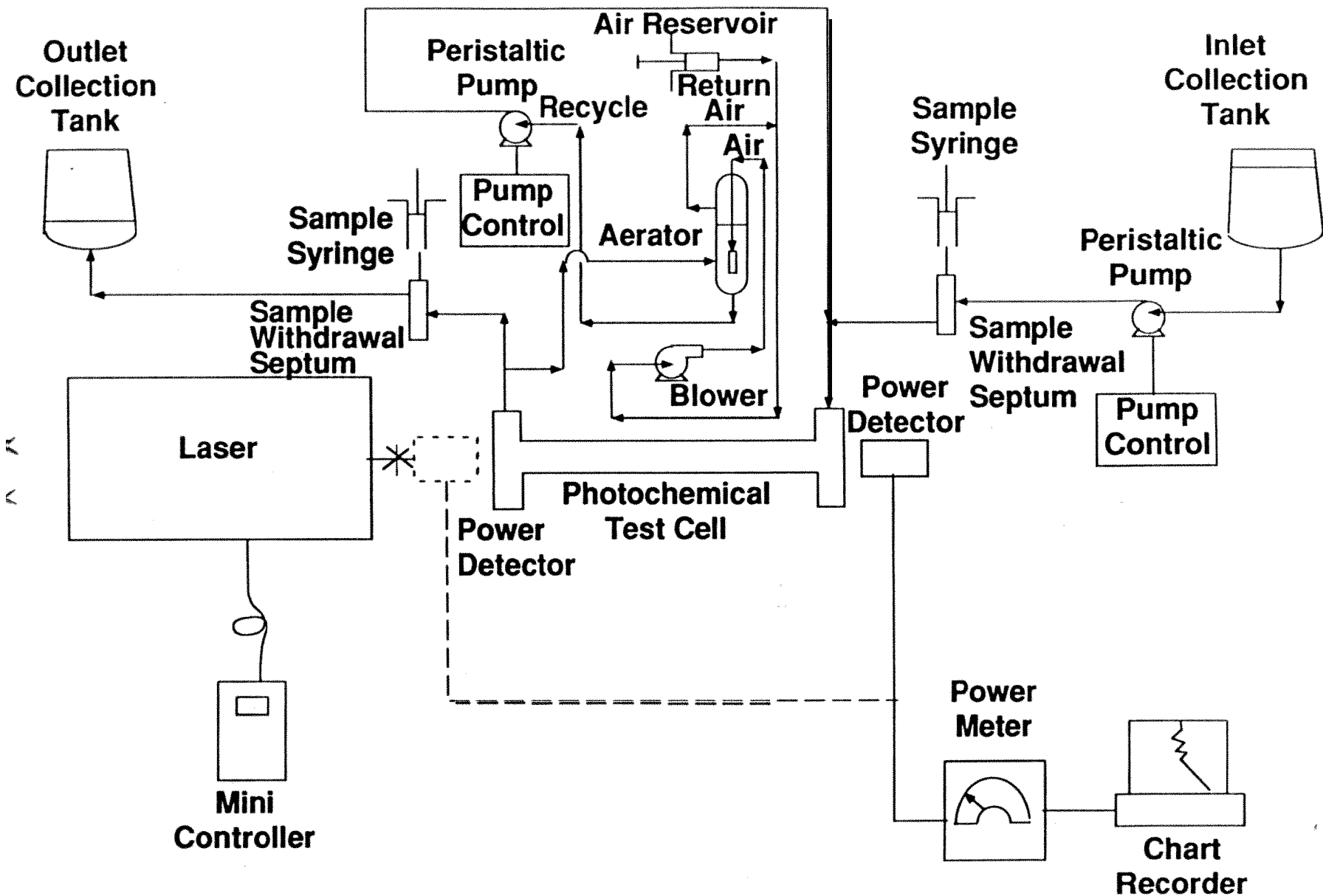


Figure 5. Schematic of Aerated Recycle Apparatus

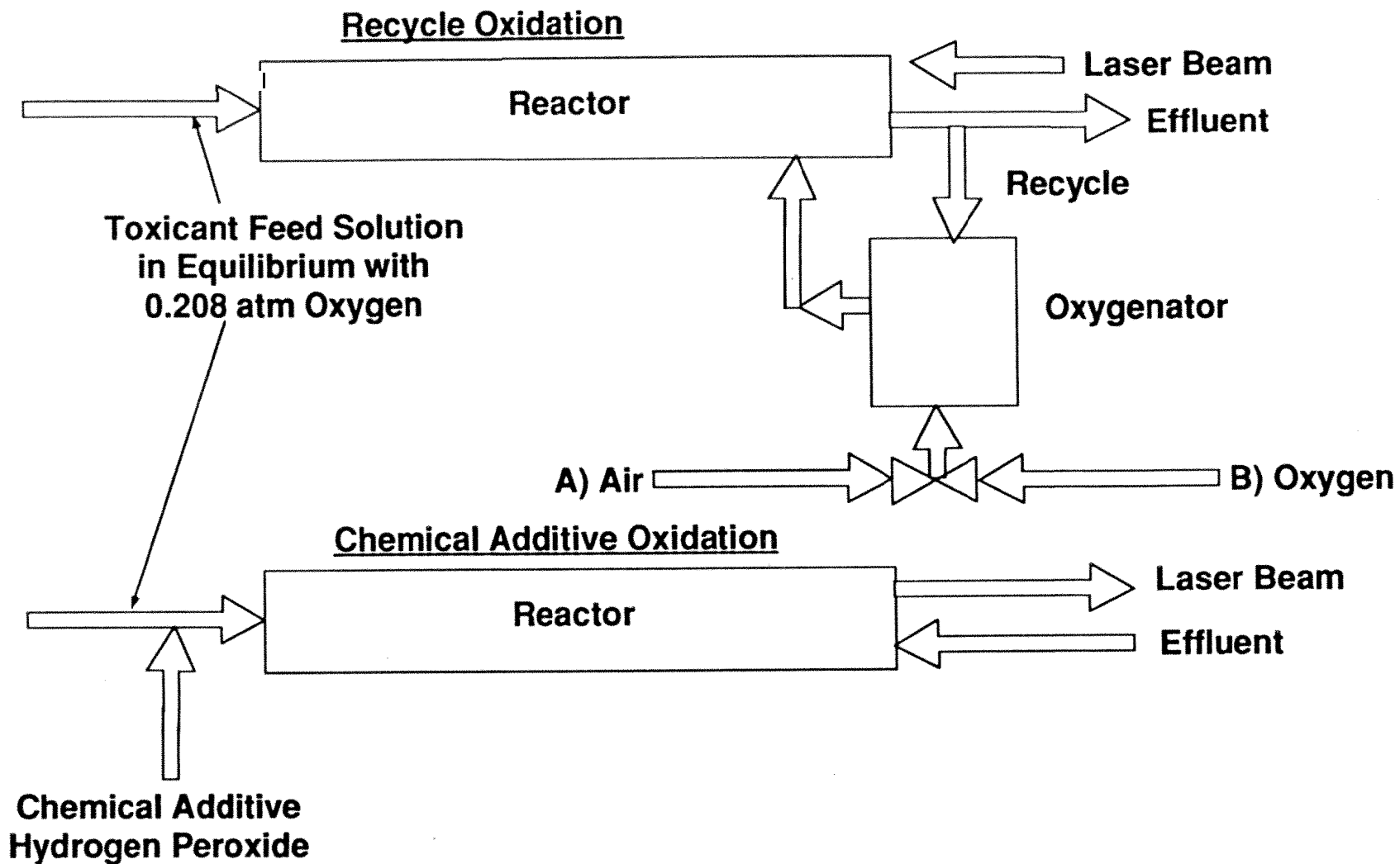


Figure 6. Process Flow Oxygenation Schemes

Each run was initiated by observing the chlorobenzene destruction without the laser on. With the laser on, to ensure steady state conditions had been achieved in the reactor, only samples collected after 80 minutes run time were used for HPLC analysis. The destruction achieved was then determined by comparing the HPLC values obtained with and without the laser irradiation.

Figure 7 presents the results obtained when investigating the different oxidation schemes. It was first found that when using sodium nitrate as a potential oxidant, no destruction occurred. It was deduced that sodium nitrate is such a strong absorber of the radiant energy at the wavelength used, that very little radiation was available to interact with the chlorobenzene. When considering air and oxygen in recycle aeration, destruction was achieved, increasing with oxygen partial pressure, but only at the expense of high irradiation dosages. These results were discouraging, however, the results obtained with hydrogen peroxide as the oxidant led to unique discoveries discussed in the next section.

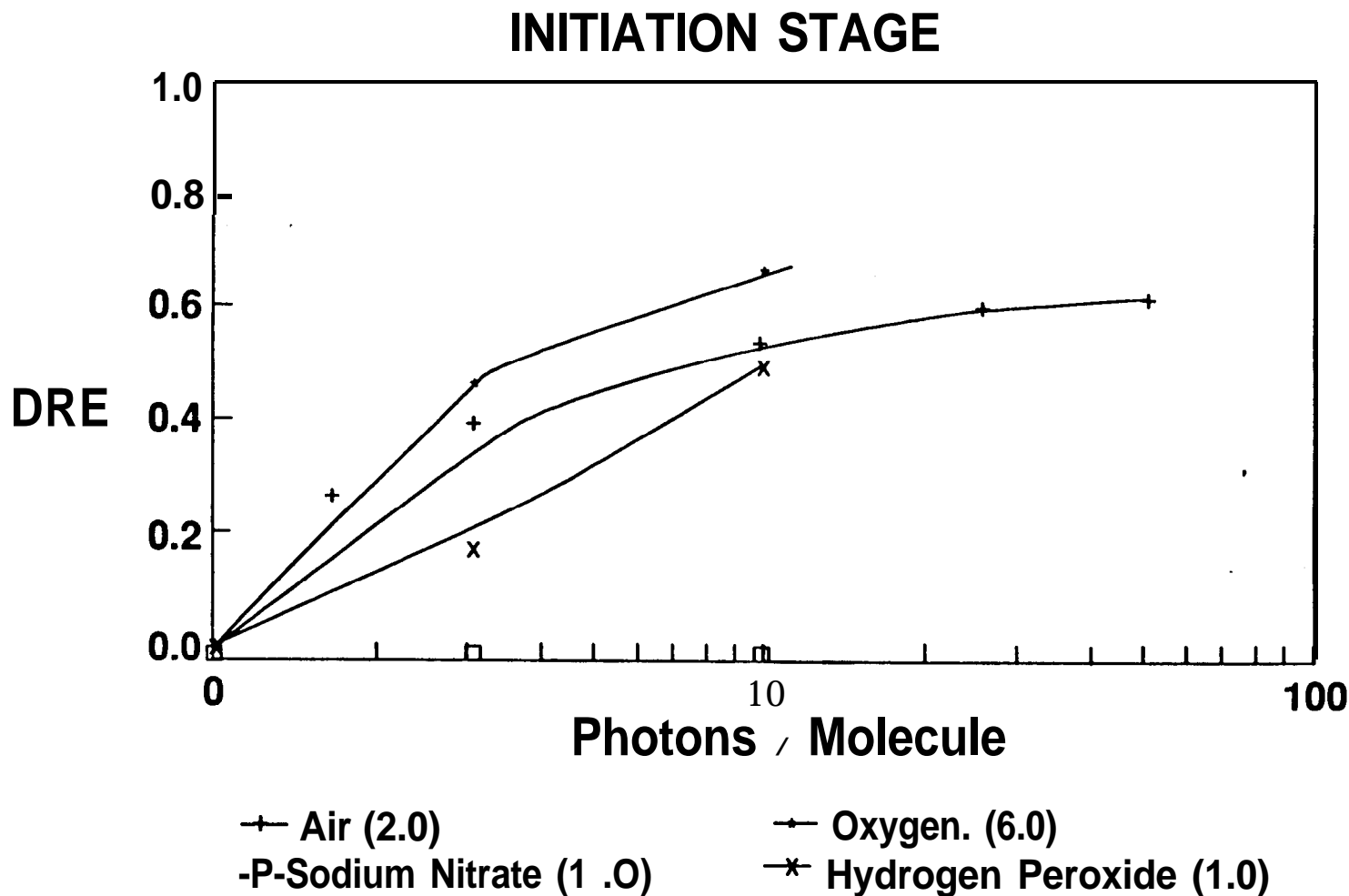
C. Hydrogen Peroxide Results

The toxic destruction using hydrogen peroxide as the oxidant (Figure 7) shows destruction equivalent to using oxygen as the oxidant. However, these data are the results of samples analyzed immediately after being collected from the reactor.

Upon review and reanalysis of some of the experimental samples, in November 1989, the following discovery was made, which was used to set the final research objectives and experimental parameters.

For most of the experiments run before November 1989 on chlorobenzene, our specific target compound, samples were only analyzed right after they were collected. However, these samples were stored in amber colored teflon lined capped vials, and so were available to be reanalyzed at a later date. The initial HPLC analyses gave results that were far from encouraging, but reanalysis and comparative review of the samples being stored in the dark to the initial results showed the destruction of the chlorobenzene had continued during sample storage. Similar results were observed for all the samples reanalyzed.

It was discovered and confirmed after several analyses that the chlorobenzene concentration and the Total Organic Carbon content of the samples sealed in the amber colored vials had diminished to extremely low levels in comparison to the initial analyses. It was subsequently substantiated that reactions leading to the toxicant destruction were continuing for extended periods of time after the initial irradiation exposure period, when varying stoichiometric concentrations of hydrogen peroxide were present in the toxic feed solution. Further experimentation and analysis showed that the



The Figure in Brackets Above Represents the Stoichiometric Oxygen Fraction Delivered.

Figure 7. Destruction of Chlorobenzene by Various Oxidation Schemes

exposure to the laser irradiation source initiates a chain reaction which continued beyond the exposure period and into a dark propagating stage which eventually leads to complete destruction of the toxicants.

A further test was carried out, by irradiating a 1 liter solution of 50 ppm chlorobenzene containing stoichiometric quantities of hydrogen peroxide. The gas evolved from the solution was collected. Calculation show that 64.5 cc's of carbon dioxide should be produced under complete oxidation conditions, presuming that water and hydrogen chloride stay in the aqueous phase. Sixty eight (68) cc's of gas were measured, and this gas was soluble in caustic solution indicating the presence of carbon dioxide.

Preliminary studies suggested that the reaction rate in the propagation stage was proportional to the irradiation dosage during exposure to the laser light source. Further, it was found that chlorobenzene and eventually the other toxicants tested were also reduced to non-toxic gaseous species of carbon dioxide and water, by observing and monitoring the total organic carbon (TOC) content of the toxicants. The TOC concentration was reduced significantly as the reaction propagated in the dark, correspondingly we also monitored and observed similar decreases in the pH as the reaction continued. These results led to examination of the LIPOD process as a laser stimulated initiation of the destruction process, which leads to a propagating destructive oxygenation reaction in the post exposure period.

After running 50 ppm chlorobenzene solutions at three different irradiation dosages of 1, 3, and 10 photons / molecule (Figure 8) and at three different stoichiometric hydrogen peroxide ratios of 0.5, 1.0 & 1.5, (Figure 9) attention was focused on the experimental parameters of 10 photons /molecule and unit stoichiometric hydrogen peroxide.

Irradiation of the chlorobenzene solutions under these conditions showed that after initial **laser** irradiation, percentage destruction was only 31%, (Table 5, Figure 10). However, continuous monitoring of the reaction process with time in the propagating phase without the light showed that greater than 98% destruction of the chlorobenzene was achieved after 115.5 hours, (Figure 11).

Similar experiments were run on six other toxic compounds (Table 5, Figure 11). The parameters were calculated for all other compounds and the experimental conditions set to achieve similar run parameters as that of the chlorobenzene case. Monitoring and analysis of these tests were similarly on an initiation and a propagation phase basis.

All **the** toxic compounds tested (except for t-dichloroethane) showed initial destructions between 18 and 30 %, while testing over time showed that the destructions achieved had increased significantly

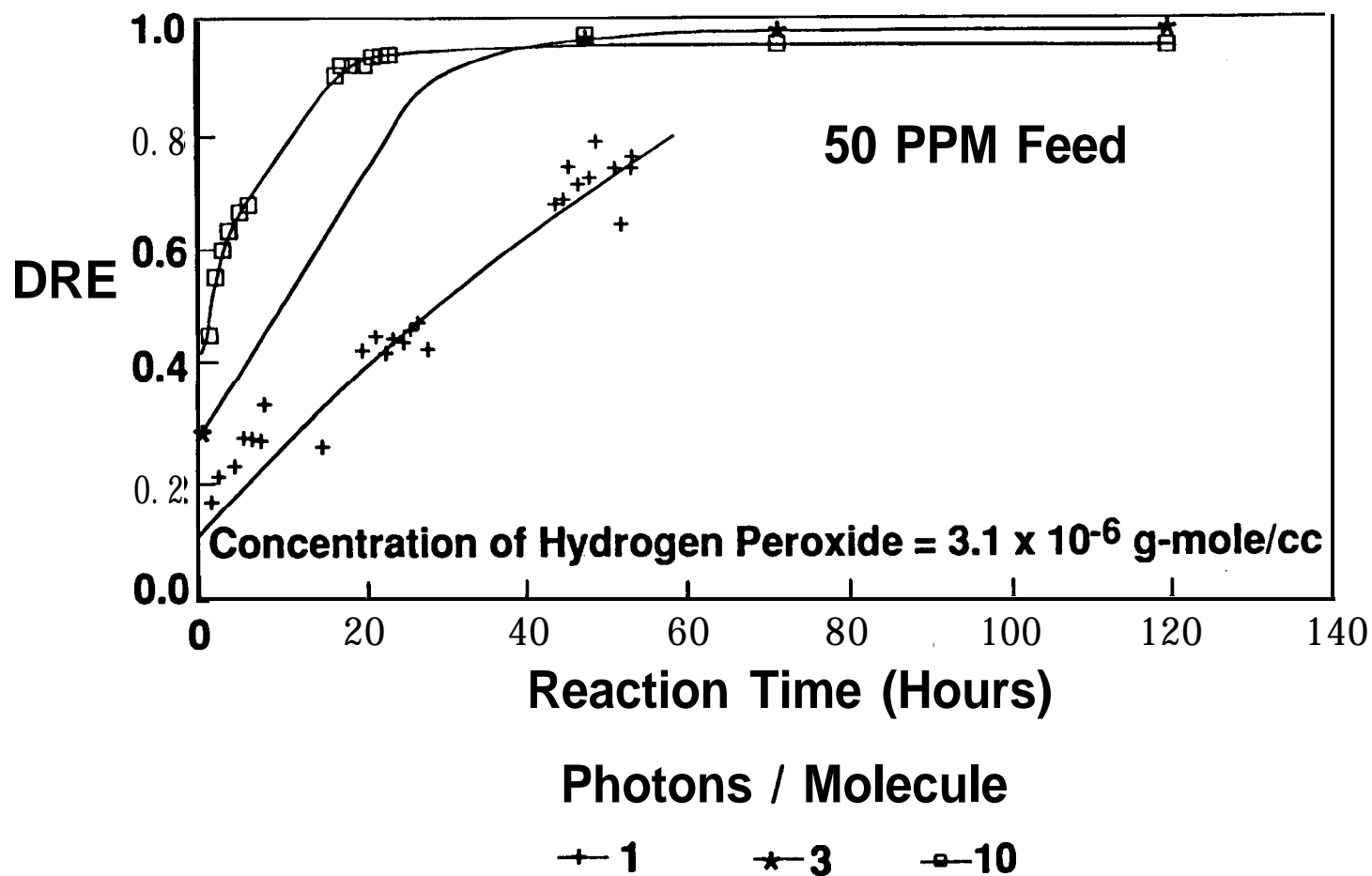


Figure 8. Impact of Irradiation Dose on Extent of Reaction

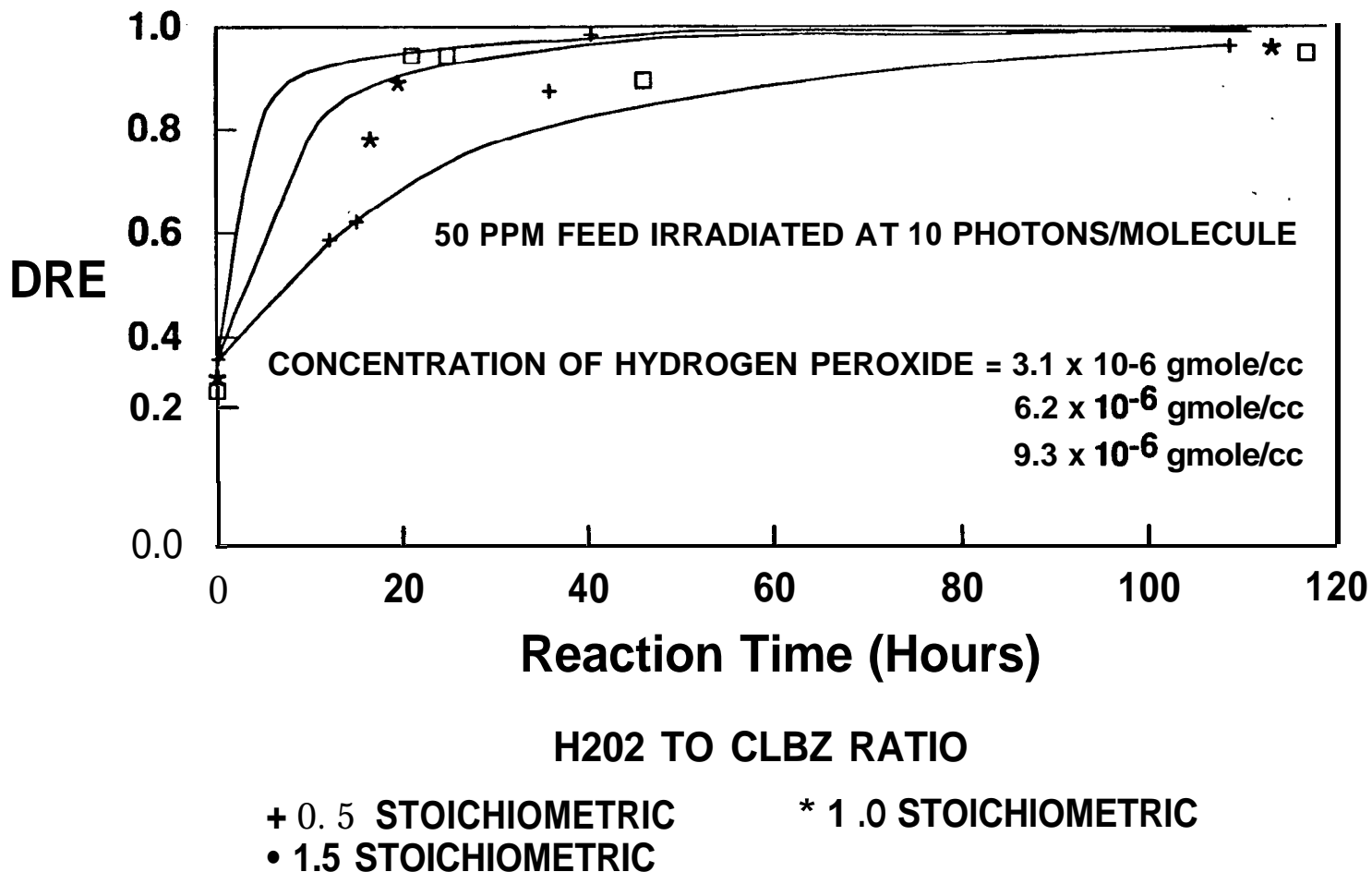


Figure 9. Impact of Hydrogen Peroxide Concentration on Reaction Rate

(HYDROGEN PEROXIDE ADDED AT 0.5, 1.0 AND 1.5 TIMES STOICHIOMETRIC RATE)

Table 5. Destruction of Various Toxic Organic Compounds by Laser

Compound	Irradiation Dose (photons/molecule)	Initiation Destruction (percent)	Propagation Time (Hr)	Final Destruction Achieved after Propagation (percent)
Benzene	10	29	96.0	91
Chlorobenzene	10	31	113.5	98
Chlorophenol	10	34	72.0	>99
Dichloroethene	10	18	624.0	88
Benzidine	10	48	288.0	88
Phenol	10	35	72.0	>99

The system was found to be dependent on an initiation and a propagation phase. Limited destruction was achieved during the photochemical initiation phase for all compounds irradiated. Greater destruction can be achieved during this phase only at the expense of applying greater irradiation dosage.

Analysis and observation of the propagation process showed significant changes in the final destruction achieved after a number of days depending on the concentration of the toxic organic compound present, the concentration of the hydrogen peroxide, and the irradiation dose applied during the initiation phase.

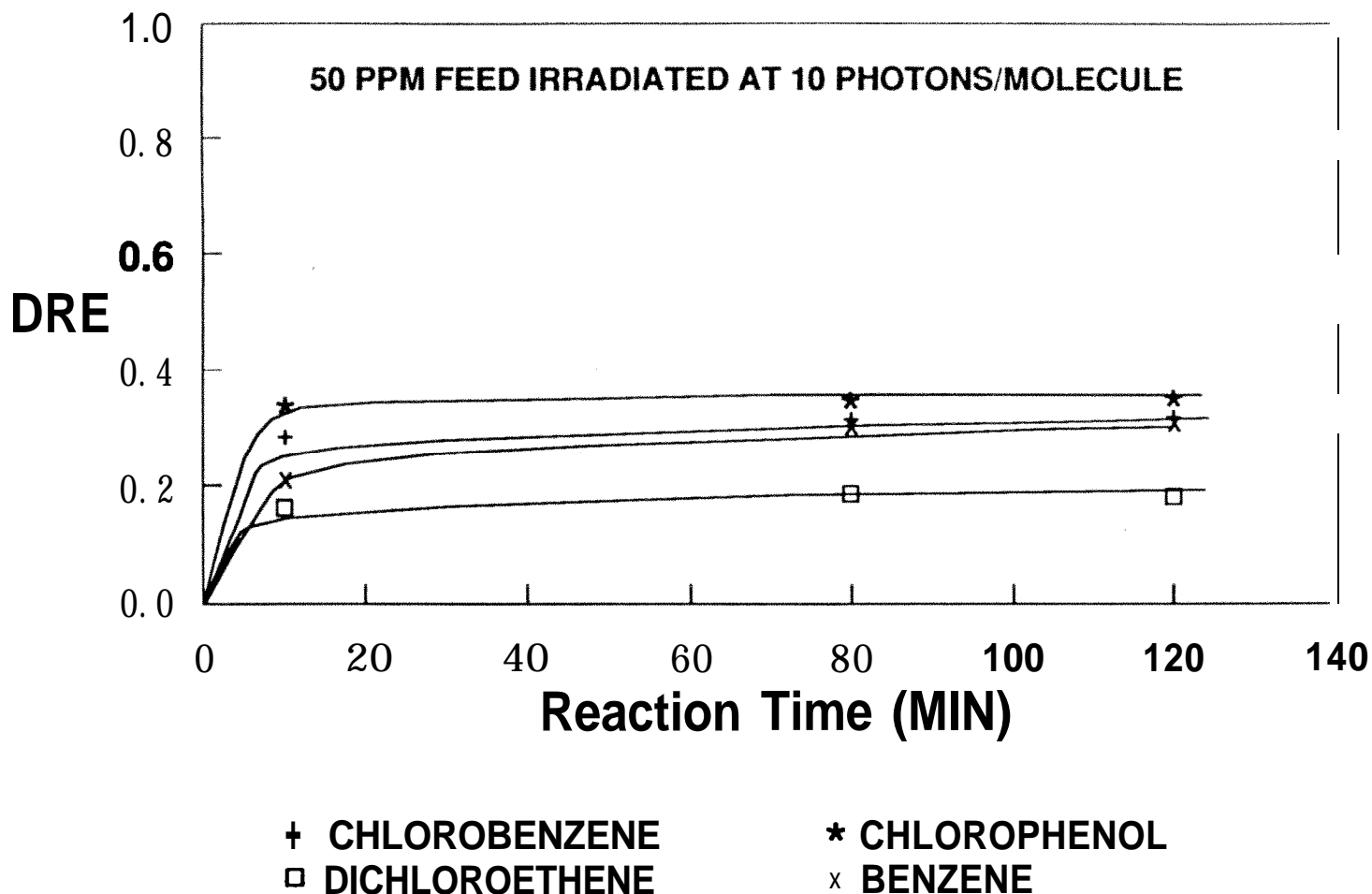
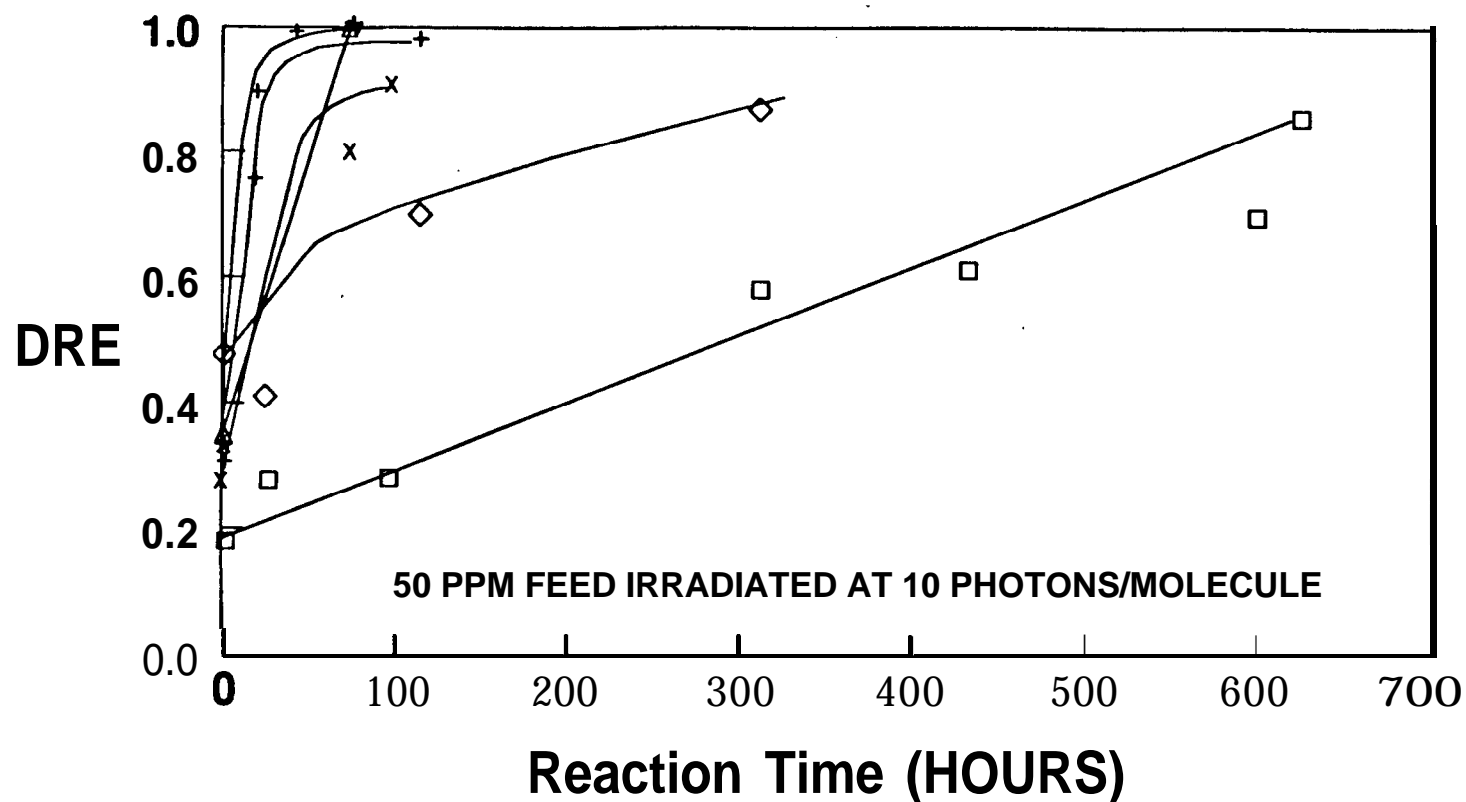


Figure 10. Extent of Reaction During the Initiation Stage

(HYDROGEN PEROXIDE ADDED AT STOICHIOMETRIC RATE)



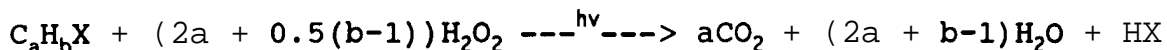
+ CHLOROBENZENE
x BENZENE

* CHLOROPHENOL
◇ BENZIDINE

□ DICHLOROETHENE
△ PHENOL

Figure 11 . Impact of Irradiation on the Reaction Rate of Several Organics During the Propagation Stage
(HYDROGEN PEROXIDE ADDED AT STOICHIOMETRIC RATE)

to greater than 95% with varying degrees of time dependency, (Table 5). Analysis and measurements using analytical tools such as HPLC, GC/MS, pH meter, TOC, and CO, absorption by caustic, have all indicated that the products of reaction are essentially carbon dioxide, water, and a halogenated acid, given by a simplified equation approximating to:



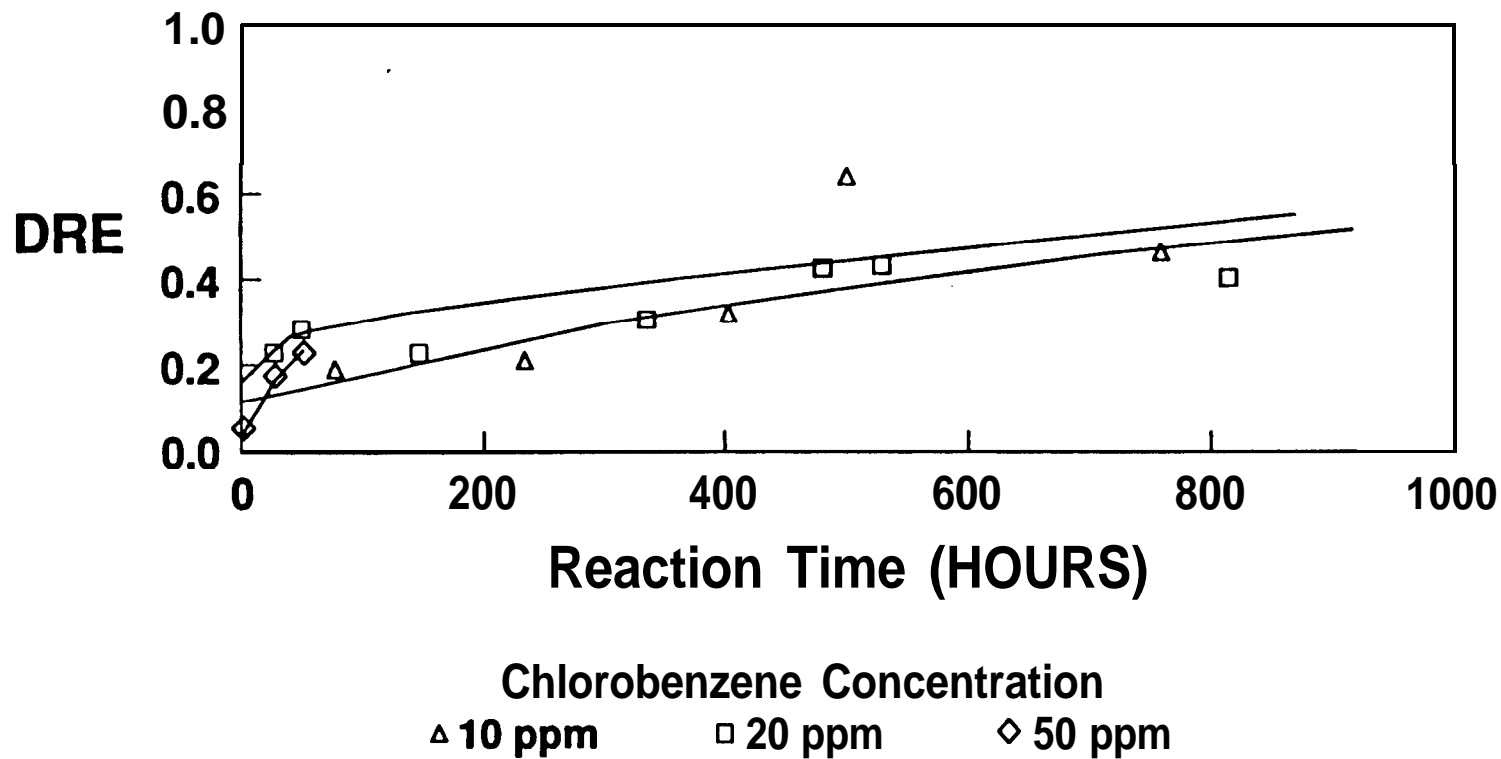
In July 1990, a series of experiments with chlorobenzene were begun, to determine the effect of toxic species concentration and irradiation dosage on the destruction efficiency of the LIPOD process. Chlorobenzene at concentrations of 10, 20, & 50 ppm (mg/L) and irradiation dosages of 1 and 10 photons / molecule were used in these experiments. The data of the results shown in (Figures 12 and 13) shows that as toxic concentration diminishes, there is an increase in the destruction in the initiation phase but there is reduction in the rate of destruction in the propagation phase.

The observations can be explained as follows. As the toxic concentration is reduced, the laser beam penetrates further into the fluid, and a greater fraction of the toxic molecules are exposed to the laser beam. However, in the dark propagating phase, the reaction becomes diffusion controlled with the reaction rate being proportional to the remaining toxic and hydrogen peroxide concentrations.

This conceptual picture is supported by the data presented in (Table 5, Figure 11), where the percent destruction achieved obtained in the initiation and propagation phases of the reaction for all the compounds studied are presented. The data show that the components which exhibit high absorption coefficients achieve the greatest amount of destruction in the initiation phase. Correspondingly those compounds with compact molecular configurations and correspondingly high diffusivities tend to show faster reaction rates in the propagation phase.

Impact of Irradiation Frequency

In order to reduce the possible reaction interferences caused by nitrates in solution, 50 ppm chlorobenzene solutions were irradiated at a higher wavelength. In the higher wavelength region, the nitrate anions in solution show negligible absorption. Figure 14 represents the data obtained in this experiment. The reaction shows a similar profile as, was obtained at the lower,, more energetic wavelength, **with the** same initiation and propagation phase reaction characteristics, but at an overall slower rate in achieving the same percent destruction achieved. This slower reaction rate in the propagation phase can be attributed to the



**Figure 12. Impact of Feed Concentration
on Reaction Rate**

(HYDROGEN PEROXIDE ADDED AT STOICHIOMETRIC RATE)
(SOLUTION IRRADIATED AT 1 PHOTON/MOLECULE)

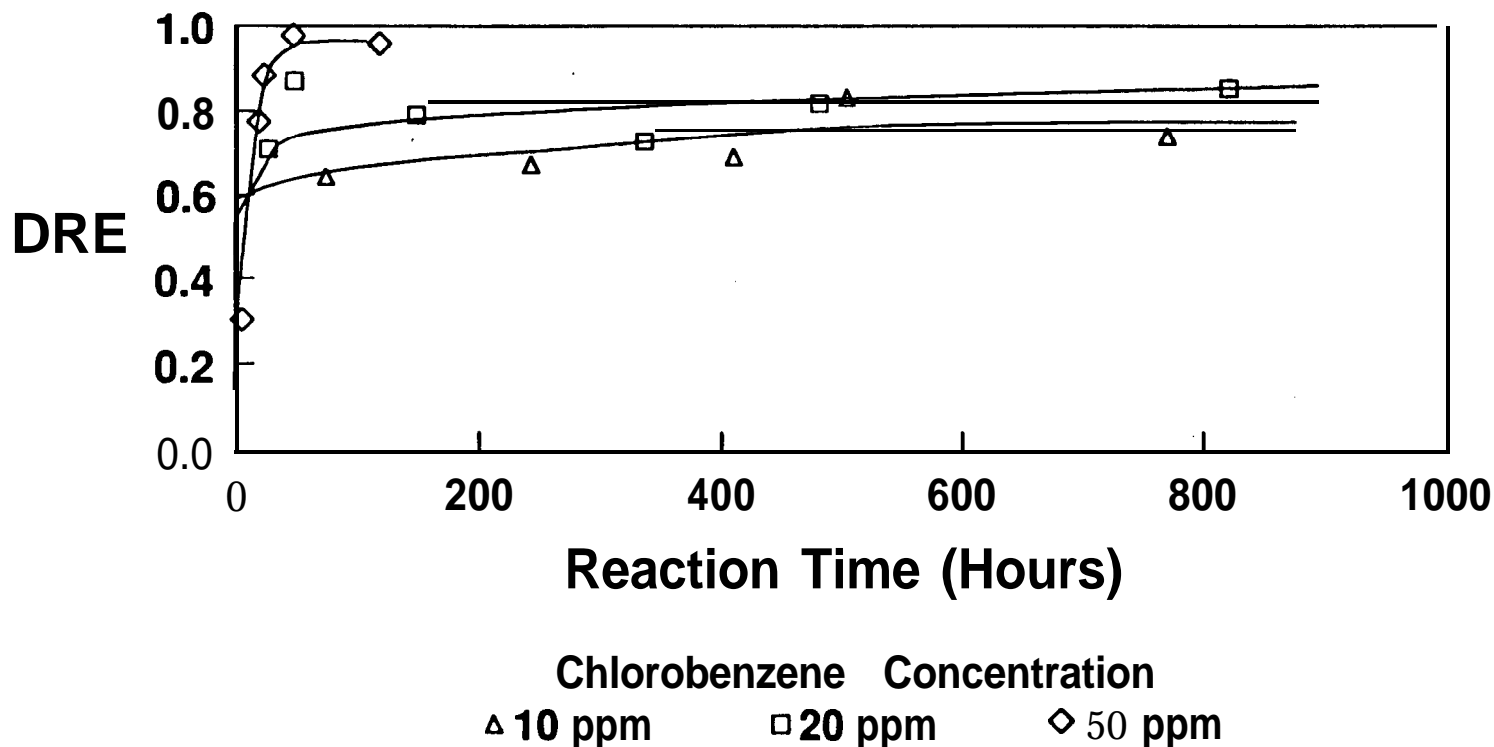


Figure 13. Impact of Feed Concentration on Reaction Rate

(HYDROGEN PEROXIDE ADDED AT STOICHIOMETRIC RATE)
(SOLUTION IRRADIATED AT 10 PHOTONS/MOLECULE)

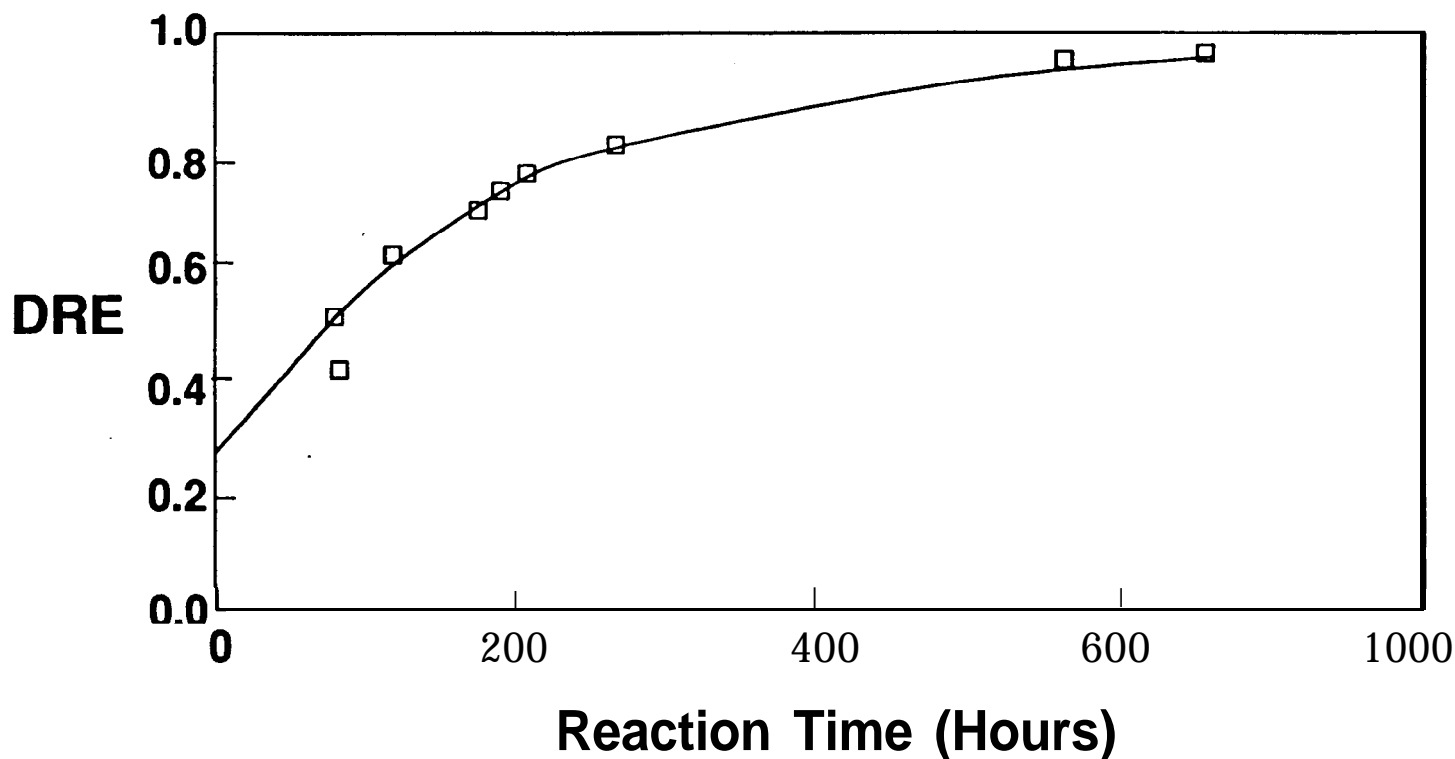


Figure 14. The Impact of Irradiation Wavelength on the Destruction of Chlorobenzene

(Hydrogen Peroxide Added at Stoichiometric Rate)
(50 PPM CLBZ Irradiated at 10 Photons/Molecule)
(Irradiation Wavelength 28.5% > Normal)

lower energetics of the photons at the higher wavelengths.

Propagating Reaction Effectiveness

To test the effectiveness of and a possible mechanism for the propagation reaction, an experiment was run in which one fourth of a 50 ppm chlorobenzene solution was irradiated and then mixed with the other three fourths of non-irradiated solution, (Figure 15). This remixed solution was monitored to determine the extent of reaction initiated by the irradiated molecules and hydrogen peroxide, to see if the fraction of irradiated molecules were energetic enough to propagate the oxygenation reaction.

Analysis of the results shown in Figure 15 shows that greater than 25% destruction was achieved. This indicated that a reaction between irradiated and non-irradiated species does take place which can eventually lead to the destruction of all species. However, the reaction rates in the propagation phase is slower than in the case when the whole fluid pool is irradiated even at one quarter of the photon /molecule dosage.

Real Waste Testing

In September 1990, the LIPOD process was tested on the leachate of a landfill from a municipal solid waste burning facility.

A sample from this waste facility was analyzed earlier in the year for its organic content, (Tables 6 and 7). The method used for the real waste testing in September was based on the total organic carbon (TOC) content of the sample after filtration with 0.45 micron filters. TOC analysis was done on the filtered samples shortly after arriving at E3I. Based on the TOC results of 1200 ppm total organic carbon in the sample, the concentration of stoichiometric hydrogen peroxide needed to totally oxidize this organic carbon content of the sample was calculated and employed for the tests.

The results of Figure 16 show that at the time of writing this report, after six days, the destruction achieved was 56 and 75 percent using five and ten photons /molecule irradiation dosages respectively, using stoichiometric hydrogen peroxide.

D. Status

The process is currently operating at the bench scale level in a system with 1 GPM capacity when treating a toxic waste stream containing 32PPM of total organic carbon in solution. The impact of absorption coefficient, irradiation dosages, toxic concentration, hydrogen peroxide concentration and the presence of common ionic species in solution on the destruction achieved and reaction rate have been determined for the six target compounds. The ability of the process to destroy a given toxic compound is

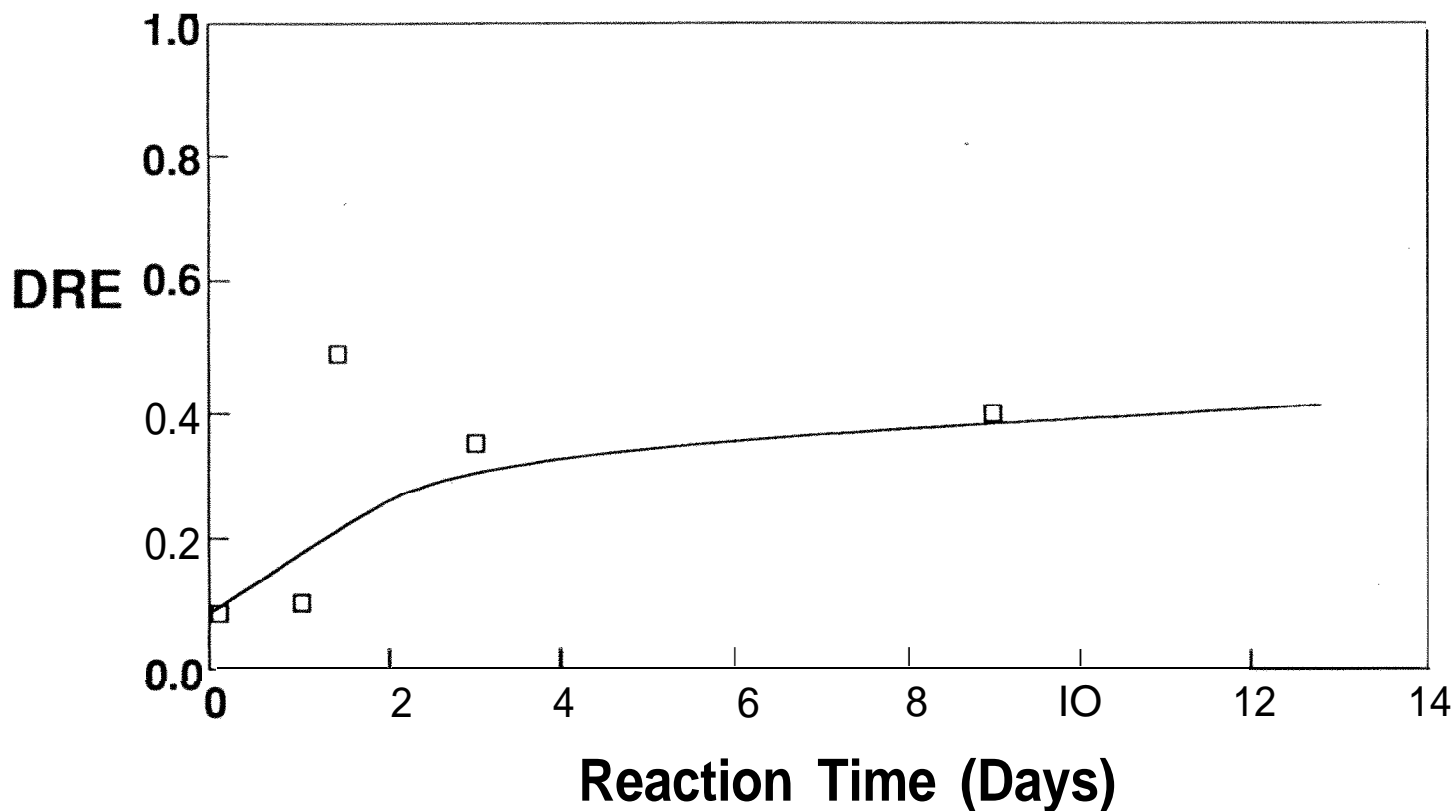


Figure 15. Impact of Irradiating a Portion of the Fluid

(50 PPM CLBZ Irradiated at 4 Photons/molecule
1 Liter of Irradiated Solution Mixed with
3 Liters of Non-Irradiated Solution)

Table 6. Semivolatile GC/MS Analysis Real Waste (6/19/89)

Compound	Concentration (mg/L)
Phenol	24.29
Benzyl alcohol	7.29
2-Methylphenol	1.49
Isophorone	1.33
Benzoic acid	162.80
Dimethyl phthalate	1.06
Diethyl phthalate	5.00
Di-n-Butyl phthalate	1.18
Nitrobenzene	125.46
2-Fluorobiphenyl	96.08
Terphenyl	102.47
2-Fluorophenol	164.37
2,4,6-Tribromophenol	210.48
Standards	Concentration (mg/L)
1,4-Dichlorobenzene	40.00
Naphthalene	40.00
Acenaphthene	40.00
Chrysene	40.00
Perylene	40.00

Table 7. Semivolatile GC/MS Analysis of Real Waste (6/28)

Compound	Concentration (mg/L)
Phenol	24.60
Benzyl alcohol	8.17
2-Methyl phenol	1.11
Isophorone	1.41
Benzoi c aci d	83.00 1
Dimethyl phthalate	
Diethyl phthalate	6.72
Di - n- Butyl phthalate	
Nitrobenzene	3.46
2-Fluorobiphenyl	3.90
Terphenyl	3.92
2-Fluorophenol	5.91
2, 4, 6 Tri bromophenol	10.37
Standards	Concentration (mg/L)
1, 4 Dichlorobenzene	40.00
Naphthalene	40.00
Acenaphthene	40.00
Chrysene	40.00
Perylene	40.00

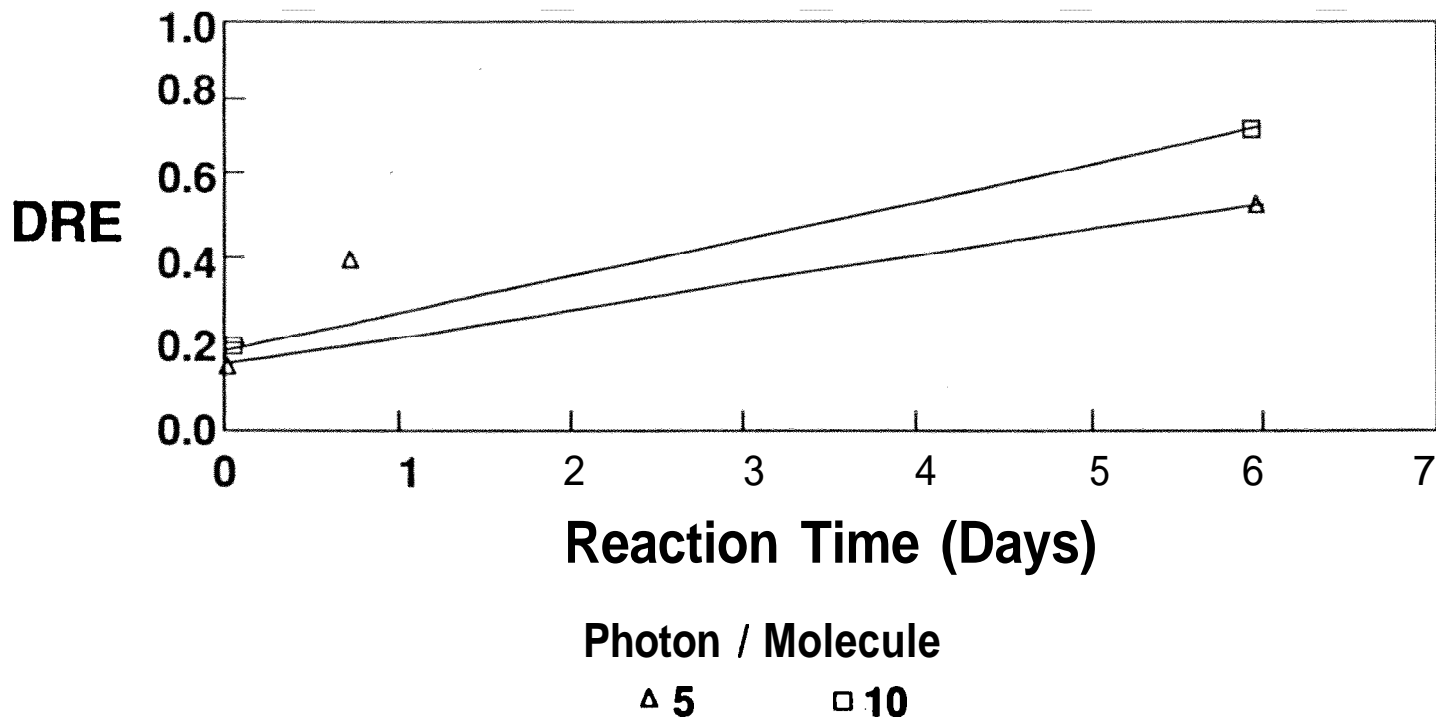


Figure 16. Destruction of MSW Leachate

(Hydrogen Peroxide at Stoichiometric Rate)
(1200 ppm Filtered with 0.45 um Filter)

measured in terms of the net destruction achieved.

Summarizing results using hydrogen peroxide as the oxidant, the impact of the hydrogen peroxide concentration on reaction kinetics is shown in Figure 10. The stoichiometric quantities of H_2O_2 used in typical applications are small. Propagation phase reaction rates increased with increasing peroxide concentration but in all cases over the ranges studied greater than 95% destruction was achieved. Figure 9 shows the impact of irradiation dosage, showing that the greater the irradiation dose received in the initiation phase of the reaction, the more rapid the destruction rate during the propagation phase. Again, complete destruction is attained in all cases, **but this** observation provides a design trade off between power cost to initiate the reaction and effluent storage reaction capital cost to contain the reaction while it proceeds to completion in the absence of light.

Figure 15 shows the impact of toxic concentration on reaction rate. Higher destruction is seen to occur during the initiation phase as the toxic concentration diminishes. This is as a consequence of the fact that the laser beam is able to penetrate further into the photochemical reactor at lower concentrations because of less absorption by a smaller number of toxic molecules. Thus as the toxic flows through the reactor it is exposed to the beam for a longer period of time and hence exits the reactor at higher levels of destruction. However, in the propagation phase, the reaction rate is species dependent, with the kinetics following the law of mass action. So, the higher toxic concentrations react more rapidly during the propagation phase of the reaction.

The impact of common ionic species normally found in waste and ground water on the **destruction achieved were** also determined. Six ionic species were examined Na^+ , Ca^{++} , Mg^{++} , Cl^- , SO_4^{2-} , and NO_3^- , of which only the nitrate showed any form of impedance on the reaction process at the 193nm wavelength employed. Nitrate ions were found to absorb the radiation at the lower wavelength, however, tests done at a higher wavelength showed that we could overcome this deficiency since the nitrate ions did not absorb at this new wavelength.

VI. Quality Assurance

A Quality Assurance Project plan for "The Laser Stimulated Photochemical Oxidative Destruction of Toxic Organics in Water" was submitted by E3I in December, 1988 to Dr. Ronald Lewis, USEPA Project Officer. A review of the QA project plan was received in February, 1989. E3I responded to the review comments in a revised QA project plan, which was sent to Dr. Lewis in July, 1989. Revision 1 of the QA project plan was accepted by the USEPA and adhered to throughout the project. As research proceeded, results directed attention toward several new areas for investigation. The work plan for the project was expanded and altered somewhat to

accommodate additional experimentation. These changes were discussed in detail and approved by the project officer. A technical systems audit of the laser project experimental process was conducted on August 29-30, 1990. The following areas of laboratory operation were reviewed for conformance to the quality assurance project plan and standard good laboratory practice:

- Standard Operating Procedures
- Sample Collection
- Analytical Methods
- Preparation of Standards
- Instrument Calibration
- Quality Control Procedures
- Preventative Maintenance
- Documentation
- Safety
- Waste Disposal
- Reporting

Laboratory and technical systems for the project were determined to be in control. Procedures and documentation were found in order.

VII Evaluation of the LIPOD Process

Based on the experimental results, the following criteria were established for the successful application of the technology:

1. The UV radiation must be at a wavelength where the energy is not significantly absorbed by the water molecules.
2. The **UV** radiation must be absorbed by the hydrogen peroxide and the toxic organic.
3. The energy of the absorbed photons must exceed the bond energy of the absorbing molecule so as to be able to cause excitation and fragmentation and thereby a reaction.
4. A source of hydroxyl radicals, such as hydrogen peroxide, must be **present** to initiate the oxidative chain reaction. When using dissolved oxygen in water as the oxidant, the effective chain reaction does not occur, and the toxic is oxidized only **at the** expense of using high dosages of UV radiation.

Aromatic and unsaturated organics, which normally appear high on the priority pollutant list, meet the above criteria and are thus good candidates for the successful application of the technology.

Table 8 shows an operating comparison between the **UV** oxidation

Table 8. Operating Comparison of UV Oxidation Processes

Process	Low Intensity UV Radiation Processes		LIPOD		High Intensity UV Radiation Processes	
Issue	Low	High	Low	High	Low	High
Irradiation Intensity (Photons/Molecule)	.005	.014	.05	2	386	1159
Input Power (Kwatt-Hr/MGal) *	27.1	79.1	13.4	53.2	371	1113
Hydrogen Peroxide Requirements (Grams/Gram "TOC")	14	990	2.4	4.8	2.4	4.8
Ozone Requirements (Gram/Gram "TOC") **	1950	2865	0	0	0	0
Power Output Power Input	.1 .1	.1 .1	.01 .01	.01 .01	.1 .1	.1 .1
Power Source	Low Pressure UV Lamp		Excimer Laser		Low Pressure UV Lamp	

• * UV lamps are 10 to 30 % efficient in electricity to light conversion and a Laser is 1% efficient.

- ** The low intensity processes require ozone in addition to hydrogen peroxide to ensure reaction completion. Input power requirements include the cost of generating ozone on-line.

processes. The **UV** processes require an oxidant, normally hydrogen peroxide, and an energy source to overcome the activation energy barrier associated with the oxidation reactions. The high intensity **UV** process uses the **UV** light source to supply the energy. The low intensity **UV** process uses a combination of the **UV** light source and ozone to supply the activation energy. A comparison of the high and low intensity **UV** radiation processes and LIPOD shows a clear advantage of the LIPOD process due to its ability to initiate a chain oxidative reaction which continues to propagate the oxidation reaction in the absence of any light. This feature could possibly allow the LIPOD process the potential of being used as an insitu "chemical" remediation process. Because the **output to input** power efficiency of the laser is less than that for a **UV lamp**, the lamp power requirements are equivalent to that for the low intensity **UV** process. However, the laser process requires far less peroxide and no ozone to accomplish the same level of destruction. Similarly, the high intensity **UV** process requires modest peroxide levels and no ozone. However, the irradiation intensity and hence the power requirements are substantially greater than in the LIPOD process. This is due mainly to the coherence of the laser beam, which allows the beam to maintain its high intensity as it moves further away from its source. It is also beam coherence and intensity that leads to the ability of the process to initiate a chain oxidation reaction. Tables 9 and 10 show cost comparisons and projections of LIPOD's costs as a function of capacity respectively.

Carbon adsorption which is the most commonly utilized technology in the final clean up of trace contaminants in aqueous waste streams and LIPOD processes have several components in common. For example, a typical 10 gpm polishing system would require that both employ the following:

- * Pumps and piping,
- * Instrumentation and controls,
- * Filtration equipment to remove potentially interfering suspended solids.

In **comparison to** carbon adsorption, however, the LIPOD process will require additional capital for the laser. For the trace amounts of aromatic compounds for which LIPOD is especially well suited, the additional capital cost will be offset by the reduced operating cost of the LIPOD process: eg. The cost will be recovered in a period of several months. Also the carbon adsorption process requires continual supply of activated carbon or alternatively the use of expensive regeneration equipment. This process also requires the disposal of spent carbon as a hazardous waste.

Based on previously acquired information, and the effectiveness of the **present** technology, it is estimated that **the** LIPOD process will

Table 9. Cost Comparison of LIPOD to other Toxic Organic Compound Removal and Destruction Processes

Basic Data

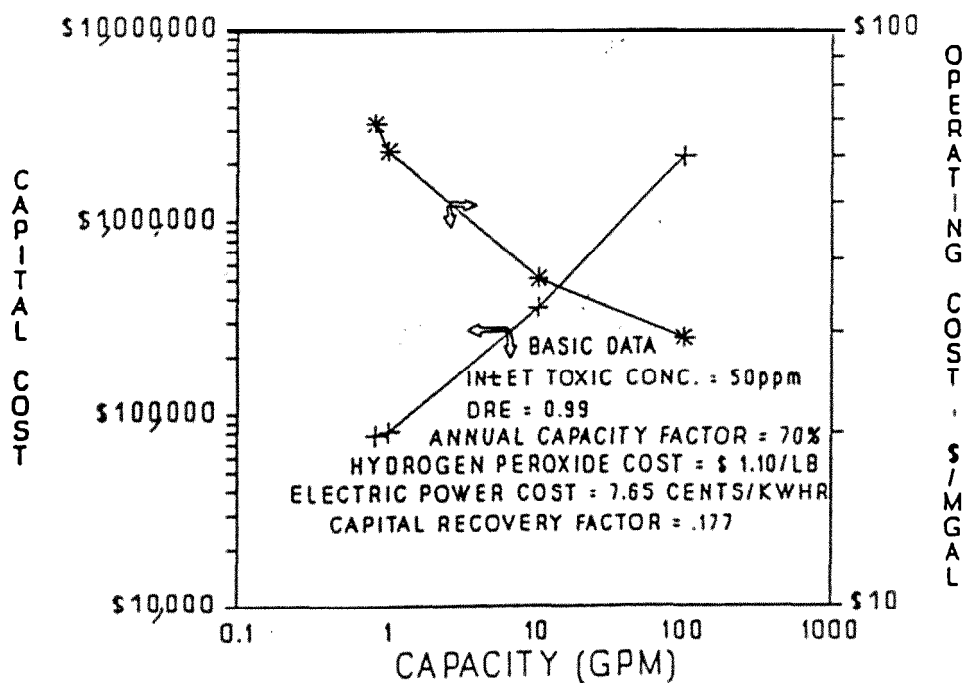
Feed flow rate	.815 GPM
Inlet chloroaromatic concentration	50 ppm
Destruction & Removal Efficiency (DRE)	.99
Annual Capacity Factor	70 percent
Carbon cost	\$ 3.00/lb
Carbon disposal cost	\$ 1.50/lb
Carbon Loading	10 mg/gram
Hydrogen Peroxide Cost	\$ 1.10/lb
Electric Power costs	7.65 cents/KWHr
UV lamp Replacement	\$ 65/lamp (65 watts lamp)
UV lamp life	1 year
Capital Recovery factor	.177 (10 years @ 10%)

Process	LIPOD	low Intensity UV radiation	High Intensity WV radiation	Carbon Adsorption
Capital Cost	\$78,000	\$55,200	\$170,000	\$30,000
Electric Power efficiency	.01	.1	.1	.95
Annual Operating & Maintenance costs (excluding labor)				
Electric Power	\$ 776	\$ 63,538	\$ 39,147	\$ 175
Peroxide	2,571	7,892	2,571	0
Laser Gases	1,969	0	0	0
Carbon Cost	0	0	0	46,000
Lamp Replacement	0	924	37,045	0
Other Chemicals	0	0	0	7,500
Maintenance & Insurance (2% of capital cost)	1,560	1,104	3,400	600
Capital recovery	<u>13,806</u>	<u>9,770</u>	<u>23,856</u>	<u>5,310</u>
Total	\$20,682	\$83,228	\$106,019	\$59,585
Cost per 1000 Gallons treated	\$68.94	\$277.43	\$353.40	\$198.61

TABLE 10. LIPOD COST AS A FUNCTION OF CAPACITY

Capacity (GPM)	1	10	100
Capital Cost	81,600	360,000	2,160,000
Annual Operating Cost (Excluding Labor and 70% operating factor)			
Electric Power	952	9,518	95,183
Peroxide	3,154	31,541	315,415
Laser Gases	2,415	24,151	241,509
Maintenance & Insurance	1,632	7,200	43,200
Capital recovery	14,443	63,720	382,320
Total	\$ 22,596	\$ 136,130	\$ 1,077,627
Cost Per 1000 Gallons Treated	\$61.42	\$37.00	\$29.29

LIPOD COST AS A FUNCTION OF CAPACITY



offer substantial savings in cost over all competing processes in the applications for which it is designed, with the per gallon treatment cost estimated not to exceed \$0.10-\$0.20.

In summary, LIPOD's favorable attributes include complete conversion of toxic organics to non-toxic species, competitive costs, and potential to provide in-situ "chemical" remediation to subsurface contamination. Unfavorable features of the process are its inability to effectively oxidize non-absorbing species such as aliphatic saturated and conjugated organic compounds, and as of yet a lack of thorough understanding of the effect of particulates on the process performance. Aliphatic compounds are not usually very toxic, and particulates may be removed by filtration.